

# *Evaluation of Remedial Alternatives Using a Reactive Transport Model: Cement Creek/Animas River*



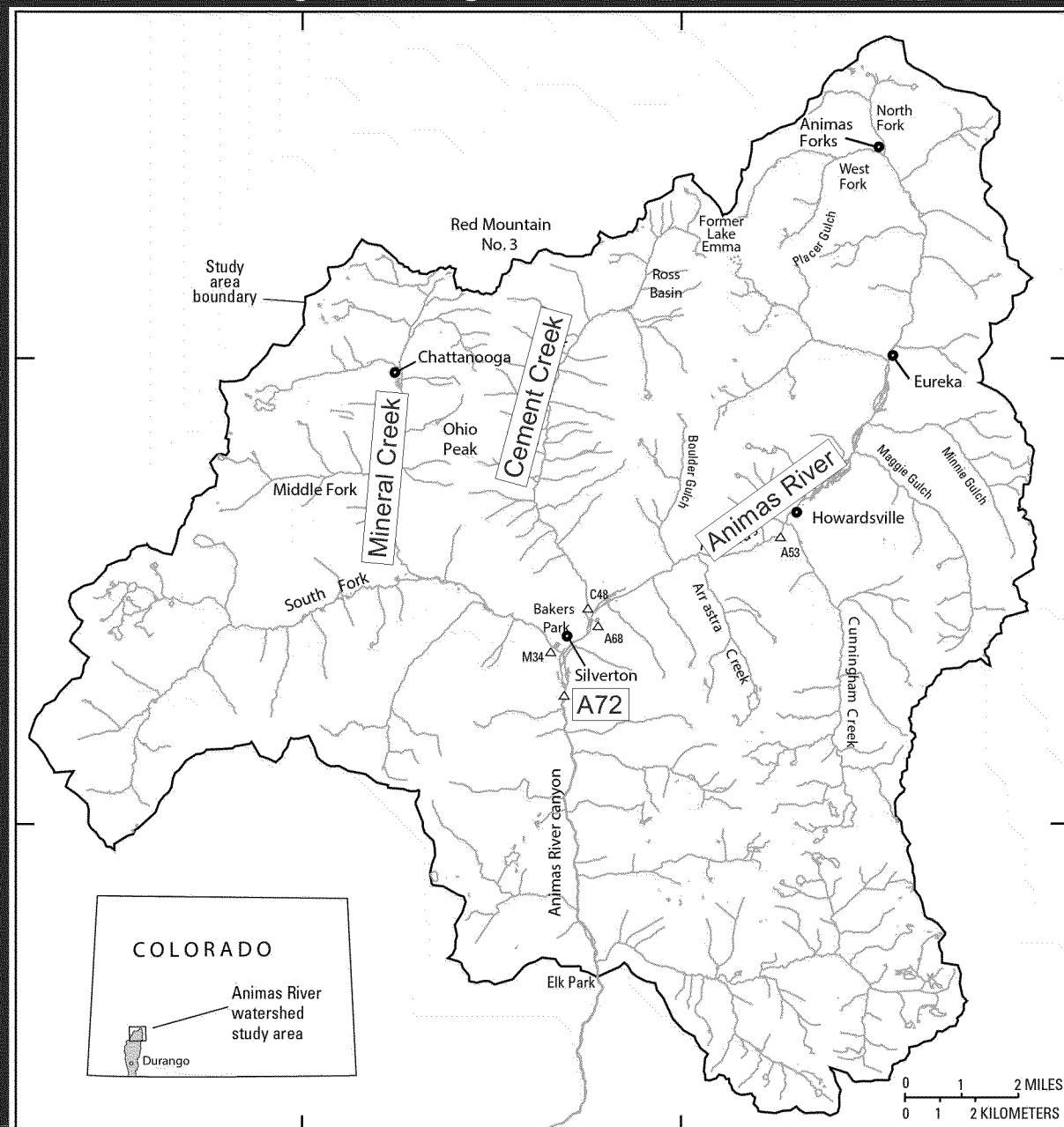
*Rob Runkel (runkel@usgs.gov)*

*U.S. Geological Survey, Toxic Substances Hydrology Program*

# Overview

- Part I: Study Objectives & Approach
- Part II: Background Info
  - Water Chemistry
  - Reactive Transport Model (OTEQ)
- Part III: Results
  - Concentrations and WQ Standards
  - Loads and Sources
  - OTEQ calibration and remedial scenarios

# Part I: Study Objectives & Approach



# Study Objective

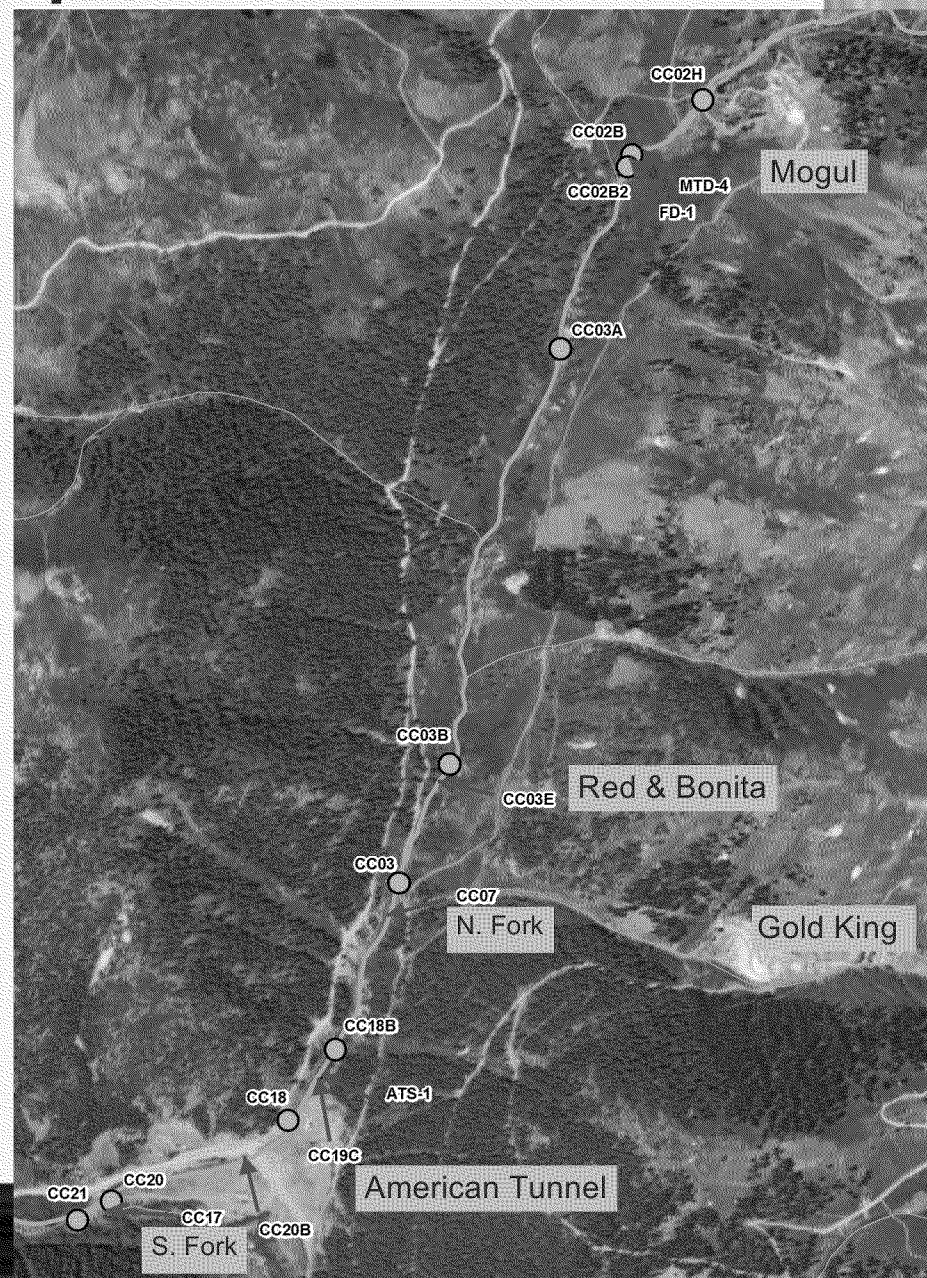
- Main Objective:  
Use a reactive transport model to evaluate remedial options for Cement Creek
- Data Requirements:
  - Synoptic data set representing “steady-state” conditions
  - Spatial profiles of streamflow and concentration
- October 2012 Synoptic

# Approach

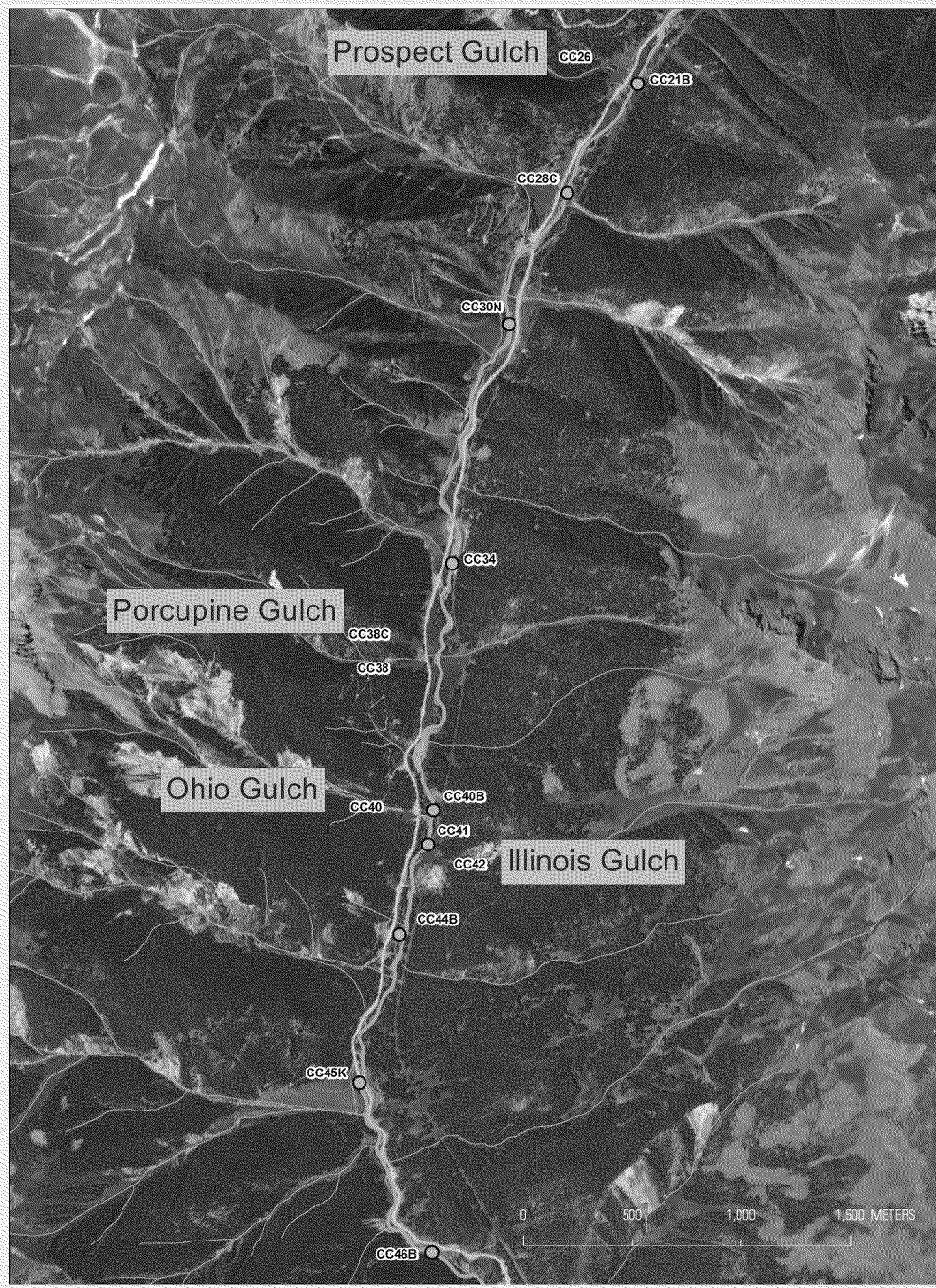
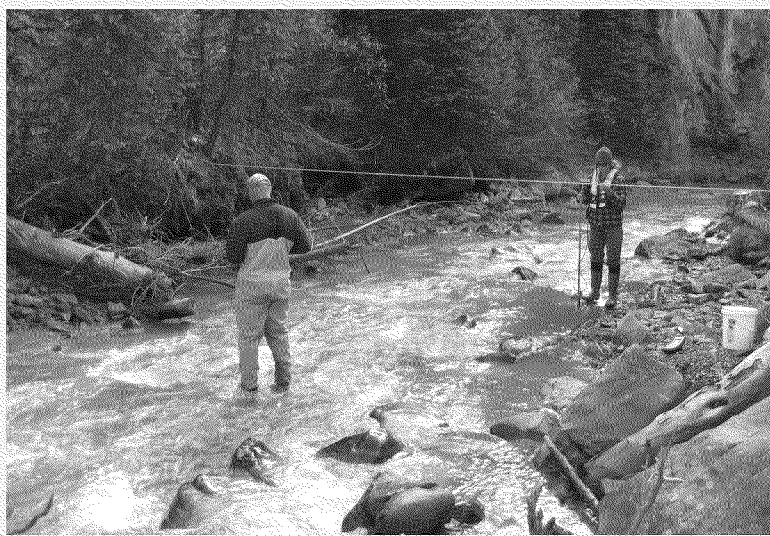
- Develop spatial profiles of streamflow & concentration
- Study Reach: Ross Basin to A72 (11.5 miles)
- October 2012:
  - Acoustic Doppler Velocimeter (ADV) to estimate streamflow
  - 2 sampling teams & 3 ADVs
  - leapfrog sampling and day-to-day overlap (replication)
- Loading analysis & modeling assume streamflow and concentration do not vary with time.

# October 2012 Sample Locations

- Chemical “snapshot”
  - 30 stream sites
  - 15 inflows
- Sampled for:
  - pH, Alkalinity
  - cations (Fe, Al, Zn...)
  - anions ( $\text{SO}_4$ , Cl...)
- leapfrog sampling
- day-to-day replication
- flow from ADV

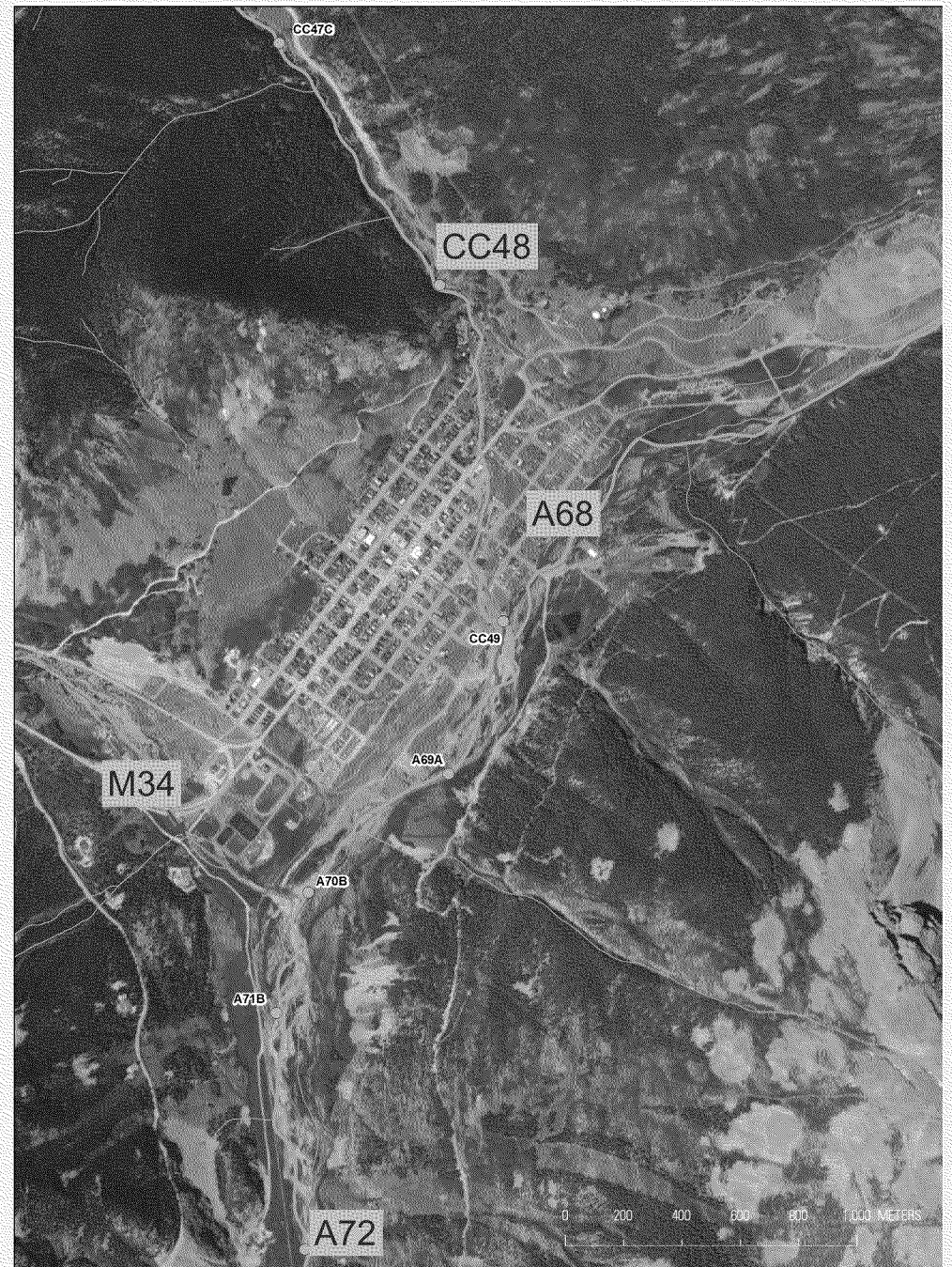
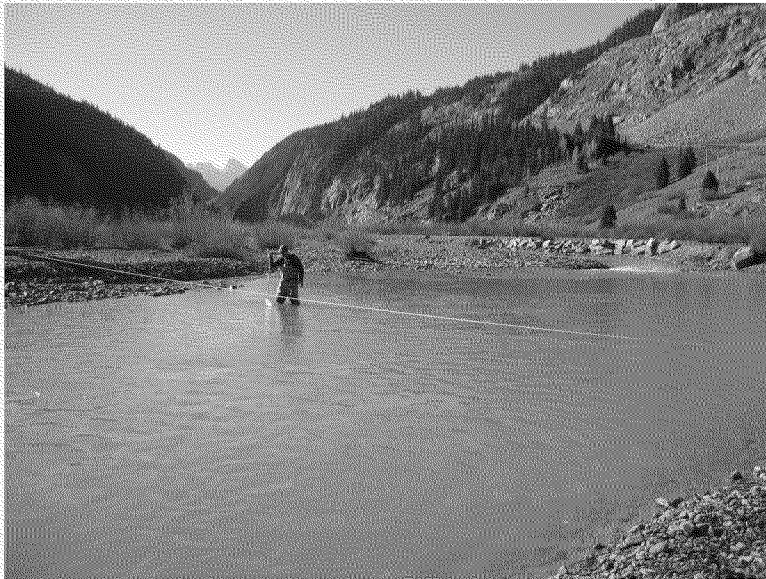


# October 2012 Sample Locations



Preliminary Results as of  
September 30, 2014

# October 2012 Sample Locations



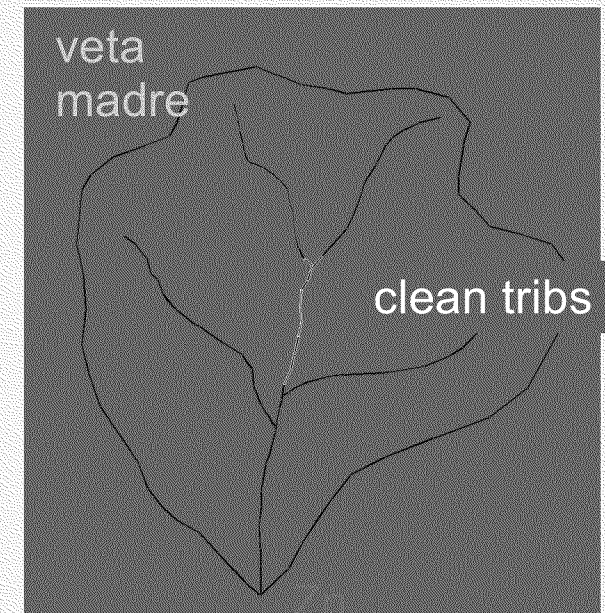
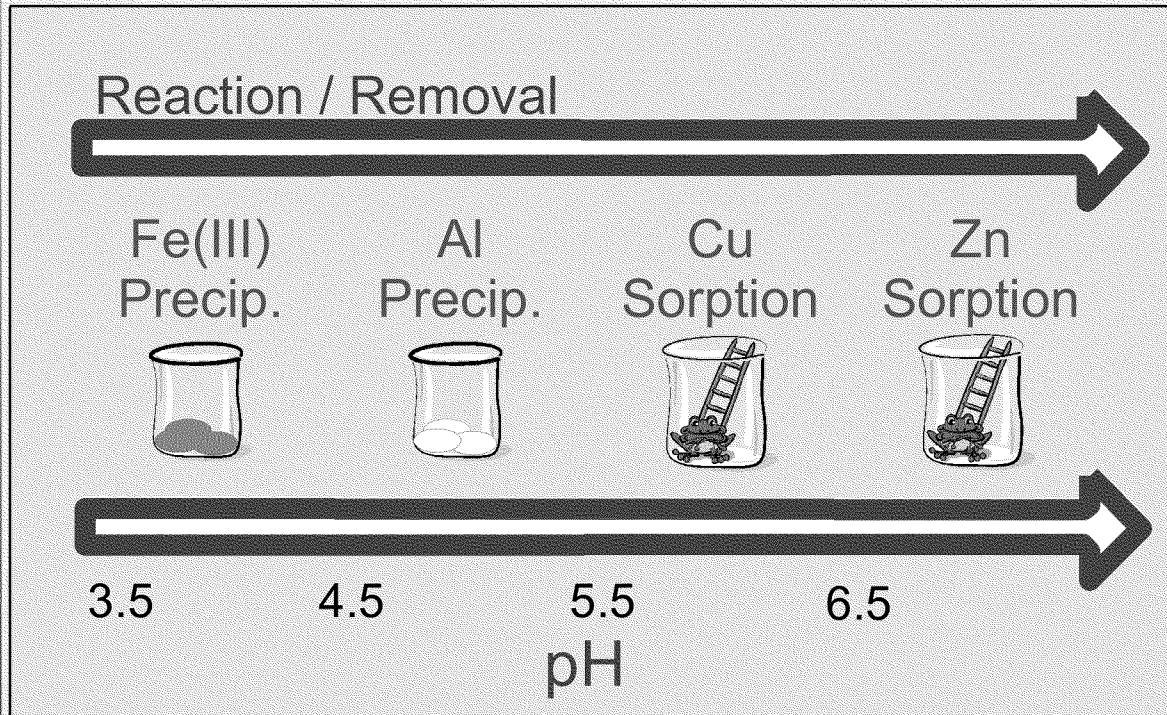
Preliminary Results as of  
September 30, 2014

## Part II: Background Info: Water Chemistry & Reactive Transport Model (OTEQ)

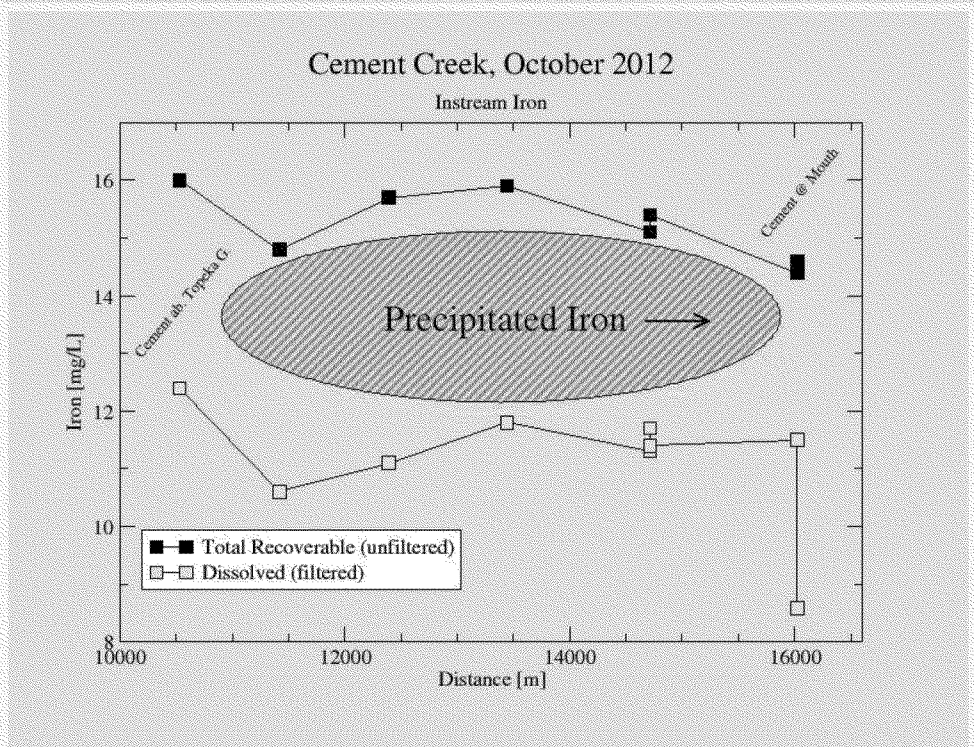
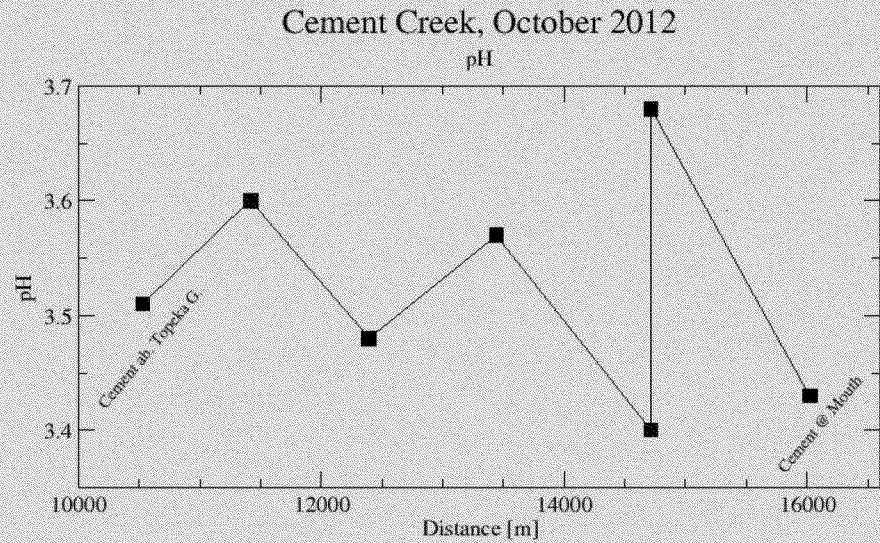
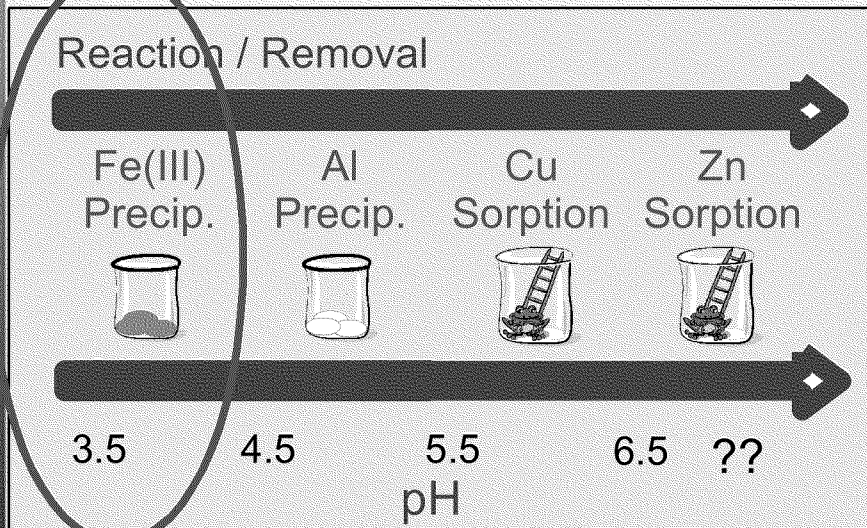
# Background: Water Chemistry

- Mineralized Ore + (Water & Oxygen)
  - Sulfuric Acid → lowers pH → elevates metals
- “Total Recoverable”
  - unfiltered sample: dissolved + solids
  - solids: Fe and Al hydroxides precipitate  
Cd, Cu, Zn, etc sorb onto Fe & Al
- “Dissolved”
  - filtered sample
  - pH-dependent solubility (low pH→high conc)

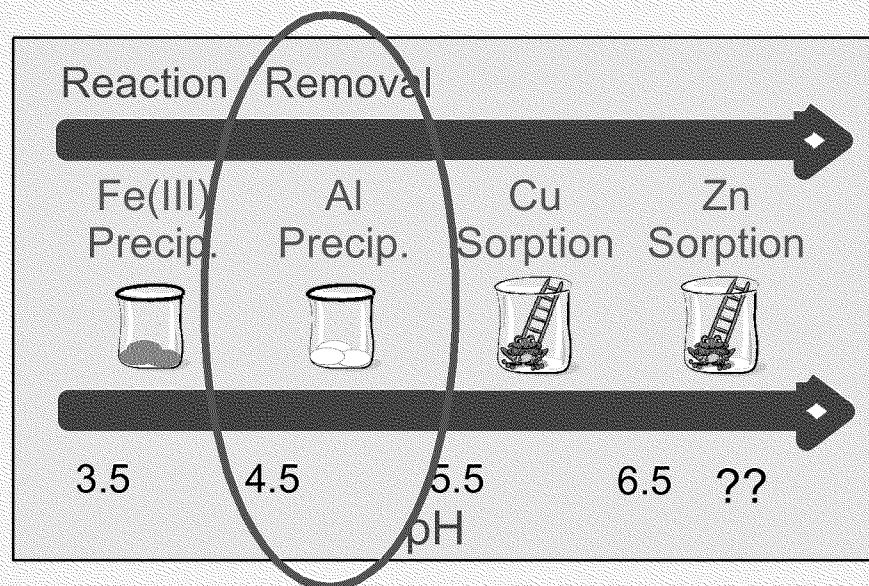
# Reactive Transport



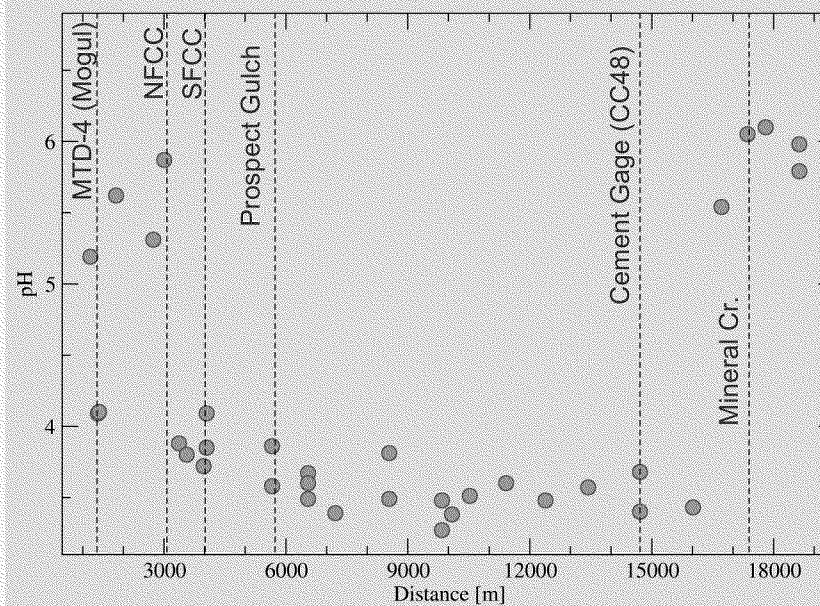
# Reactive Transport



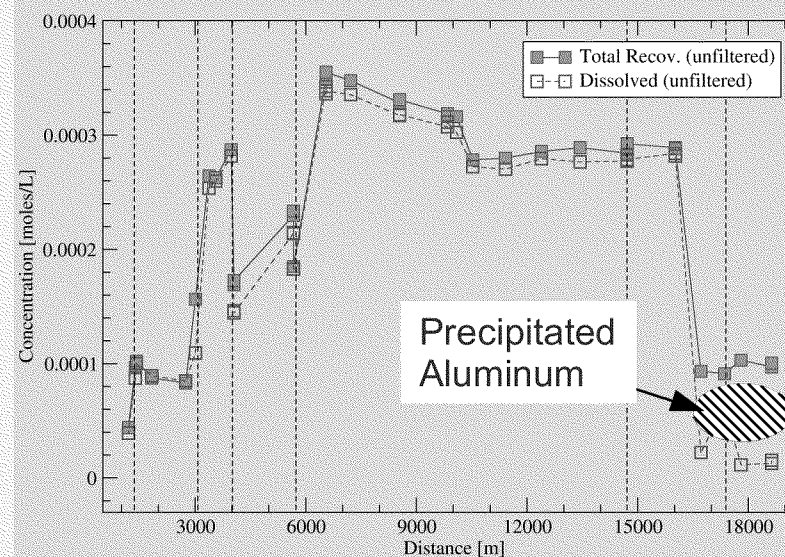
# Reactive Transport



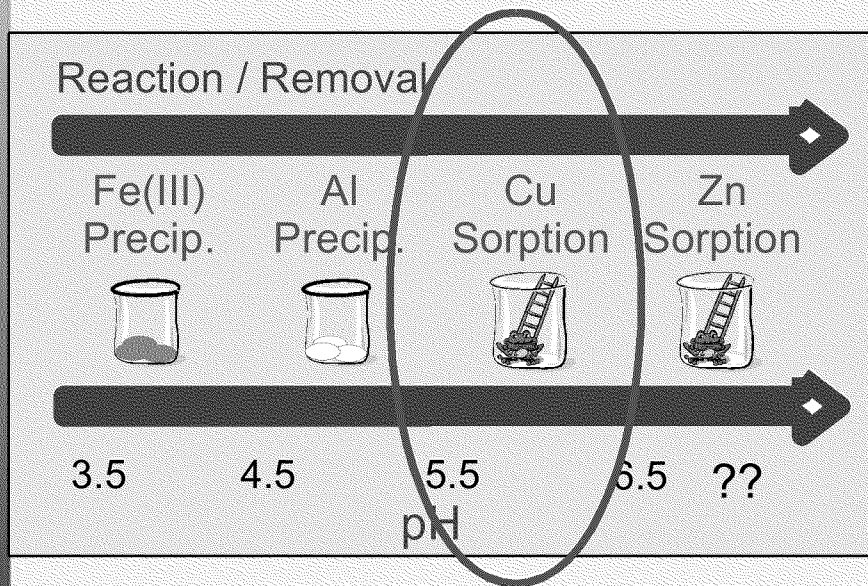
pH, October 2012



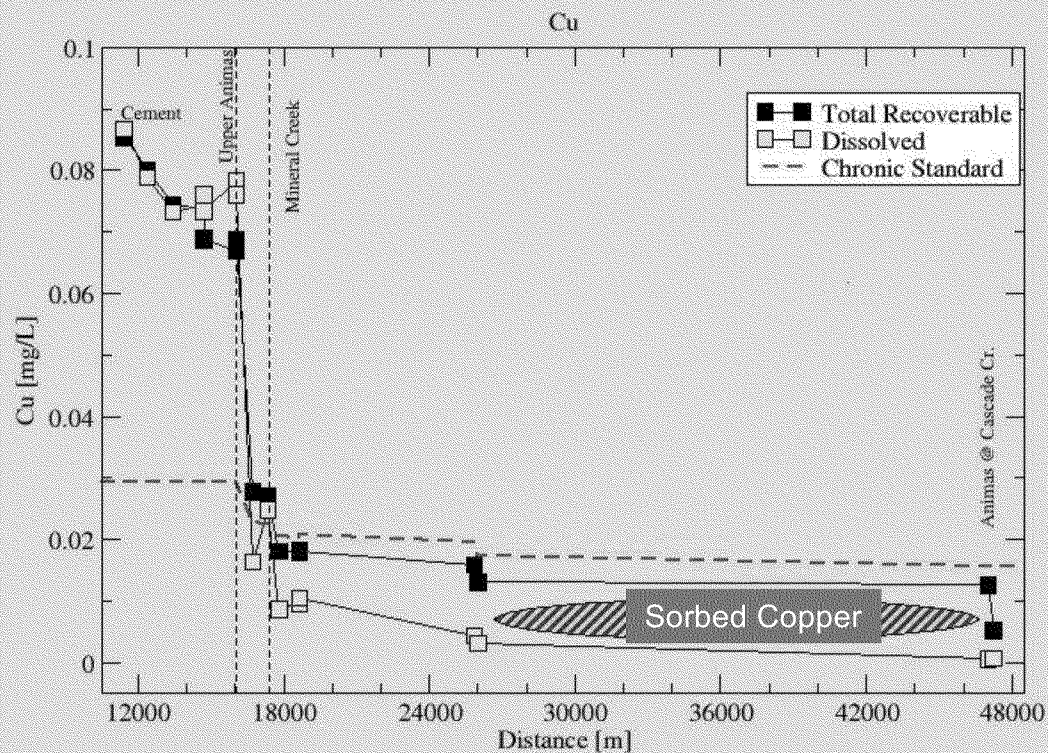
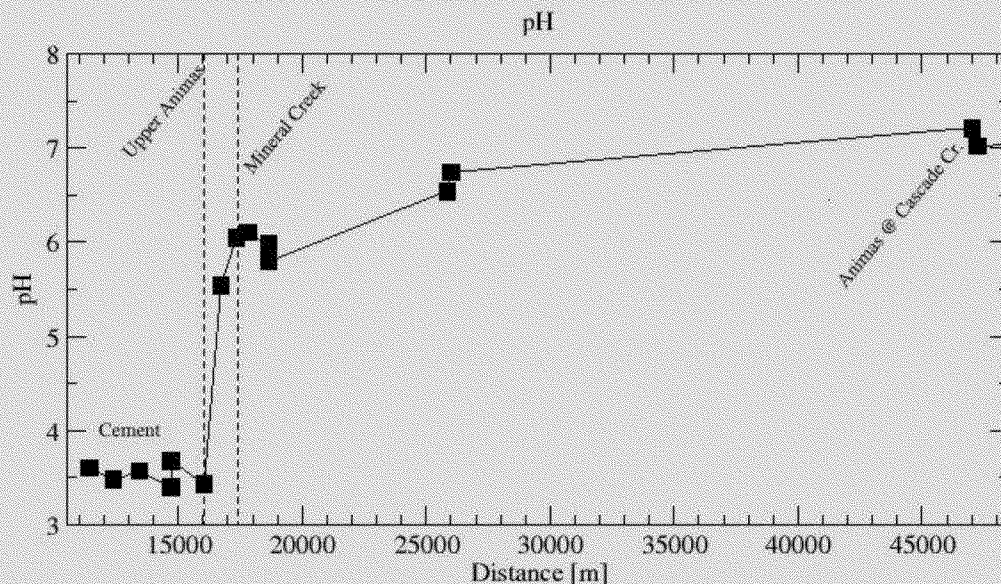
Aluminum, October 2012



# Reactive Transport



Cement Creek/Animas R., October 2012



# Reactive Transport

Reaction / Removal

Fe(III)  
Precip.



Al  
Precip.



Cu  
Sorption



Zn  
Sorption



3.5

4.5

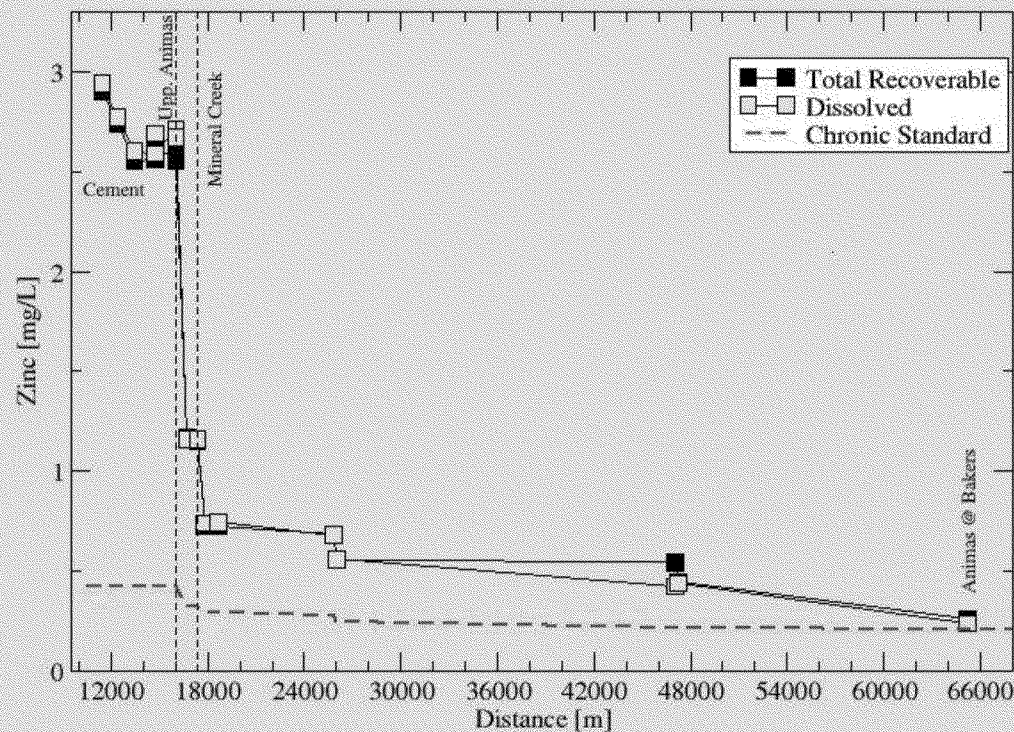
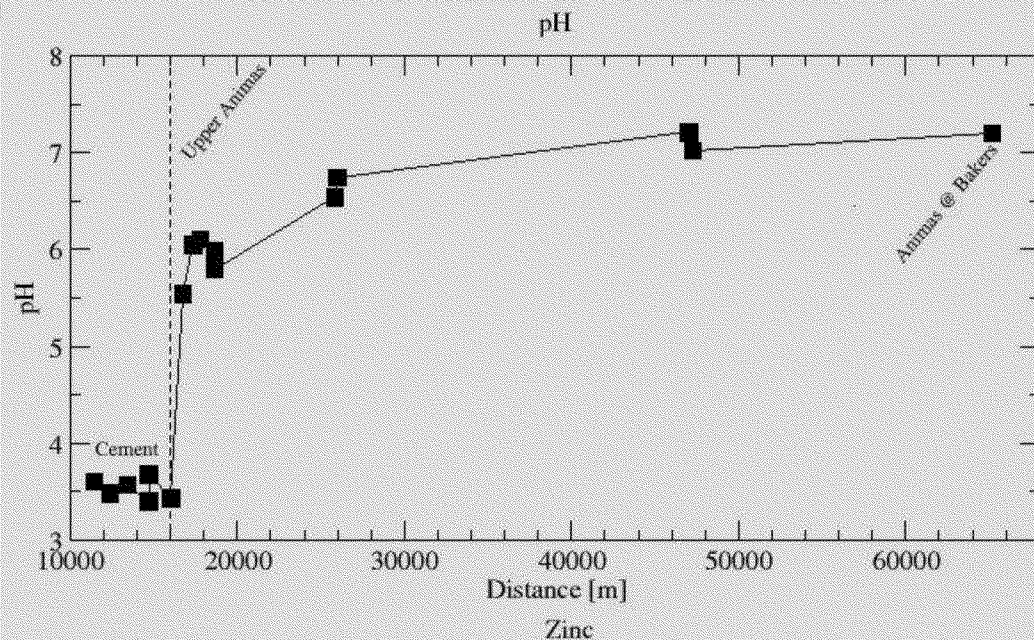
5.5

6.5

??

pH

Cement Creek/Animas R., October 2012



# Reactive Transport



→ Quantify interplay between:

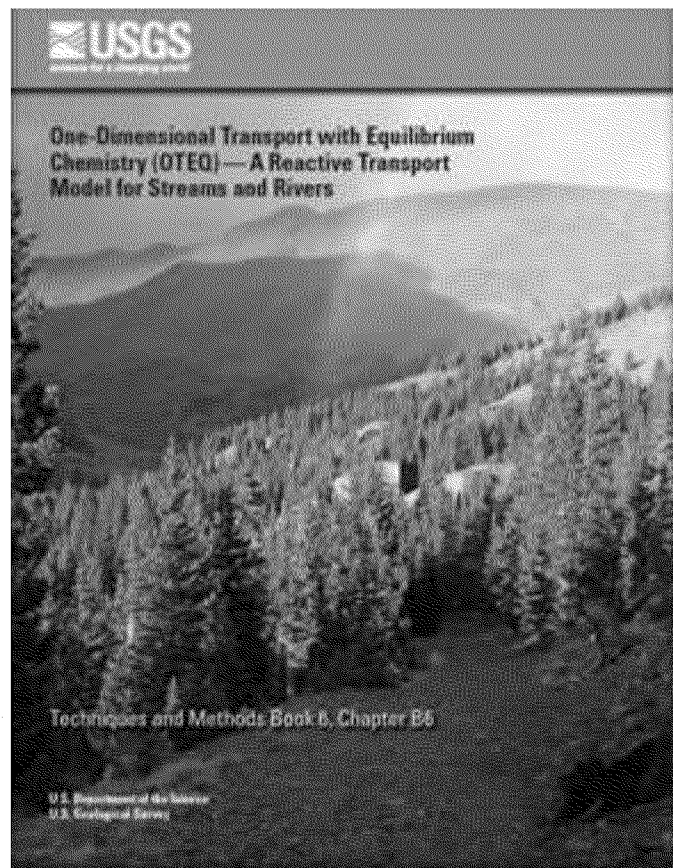
*Hydrology:* Advection, Dispersion, Storage, Inflow

*Geochemistry:* Precip./Dissolution, Sorption, pH

→ OTEQ: One-dimensional Transport w/ Equilibrium Chemistry

# OTEQ:

## One-dimensional Transport w/ **E**quilibrium Chemistry



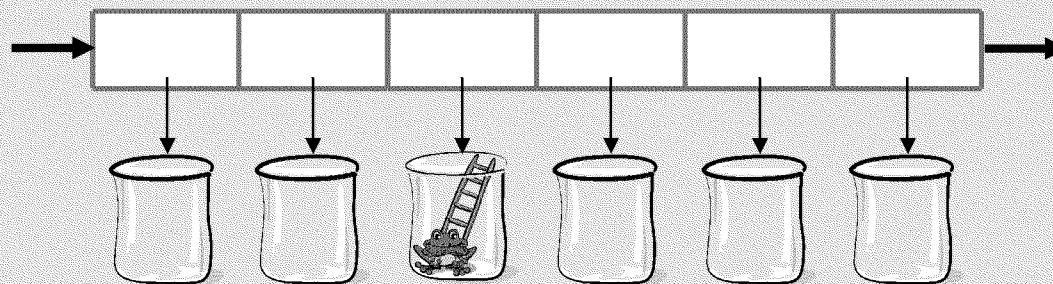
Transport (OTIS)

$$\frac{\partial C}{\partial t} = -\frac{Q\partial C}{A\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_{LIN}}{A}(C_L - C) + \alpha(C_S - C)$$

= Advection + Dispersion + Inflow + Storage

&

Equilibrium Chemistry (MINTEQA2)

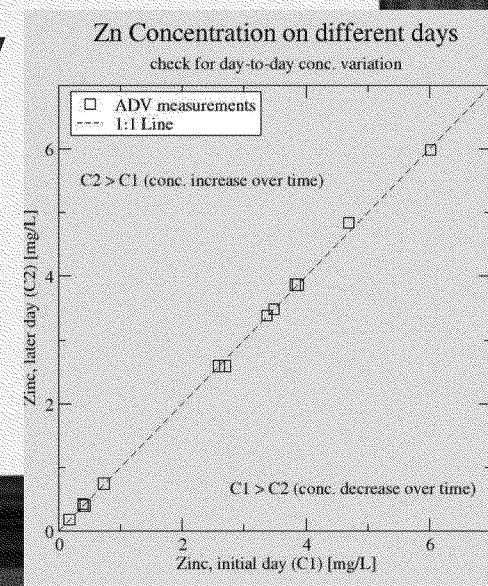


<http://water.usgs.gov/software/OTEQ>

# Part III: Results

# October 2012: Data Set Quality Assurance

- Loading analysis & modeling assume streamflow and concentration do not vary with time (Steady State)
- Data “Backbone” – Spatial Streamflow Profile
  - Essential starting point for loading analysis & modeling
  - leapfrog approach indicates streamflow was ~Steady
  - Multiple means of estimating streamflow provide redundancy; mass balance calculations used to develop spatial flow profile.
- Multiple observations of concentration provided by leapfrog approach also indicate steady-state



# Part III: Results

## Concentrations and Water Quality Standards

Above std, top to Bakers Bridge:

**Al, Cd, Zn**

Above std, top to Cascade Cr:

**Fe**

Above std, Mogul to Mineral:

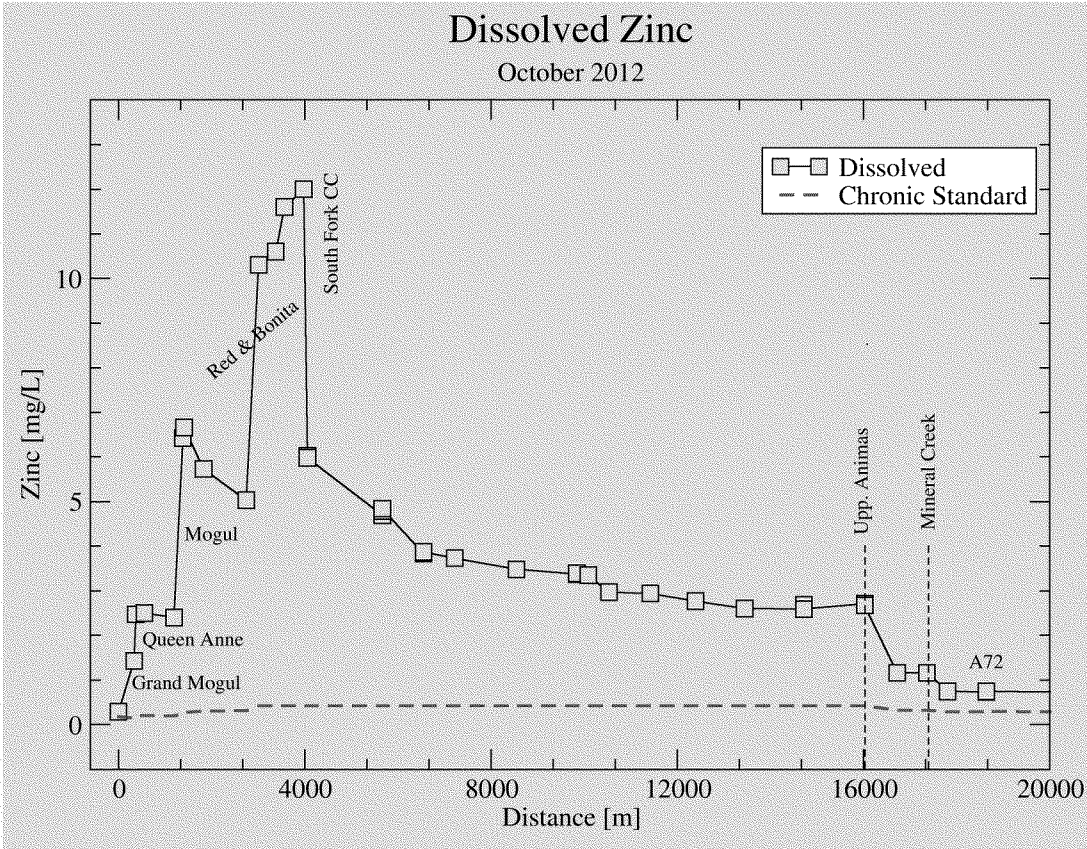
**Mn**

Above std, top to cement mouth:

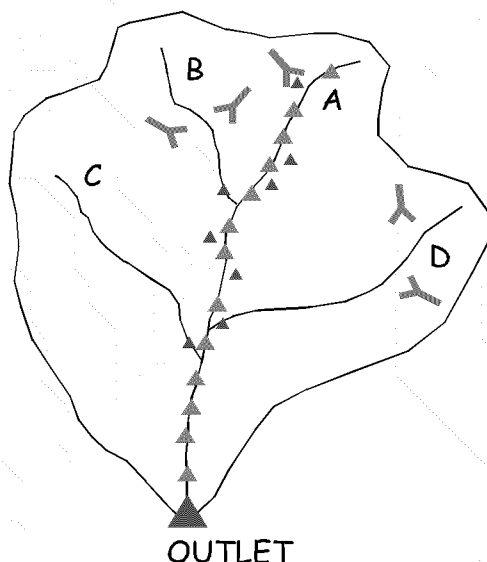
**Cu**

Above std, sub1 to cement mouth:

**Pb**



## Part III: Results – Loads & Sources



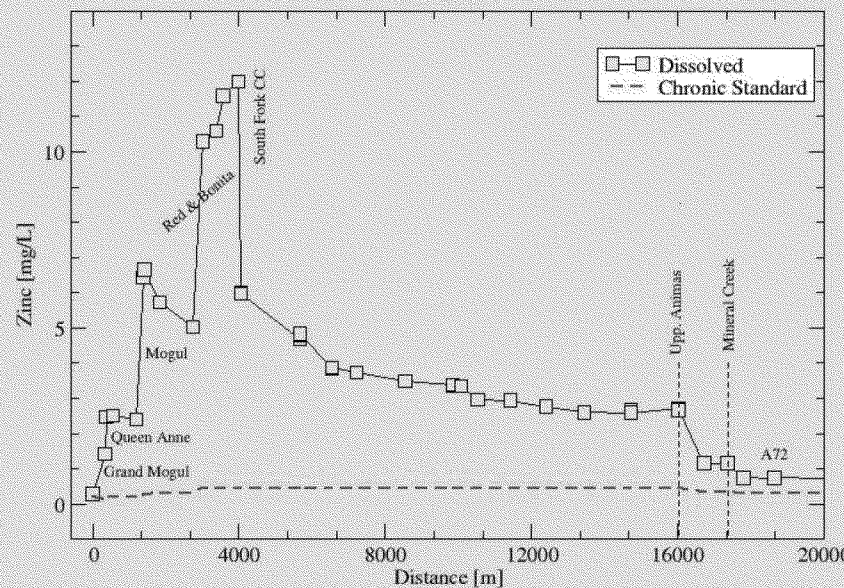
Synoptic Sampling,  
October 2-4, 2012

- Synoptic Study:
  - Spatial profiles of Streamflow & Conc.
- Load (mass / time) = flow \* concentration
- → Spatial profiles of mass load
- + changes in load used to identify source areas

# Part IV: Results – Loads & Sources

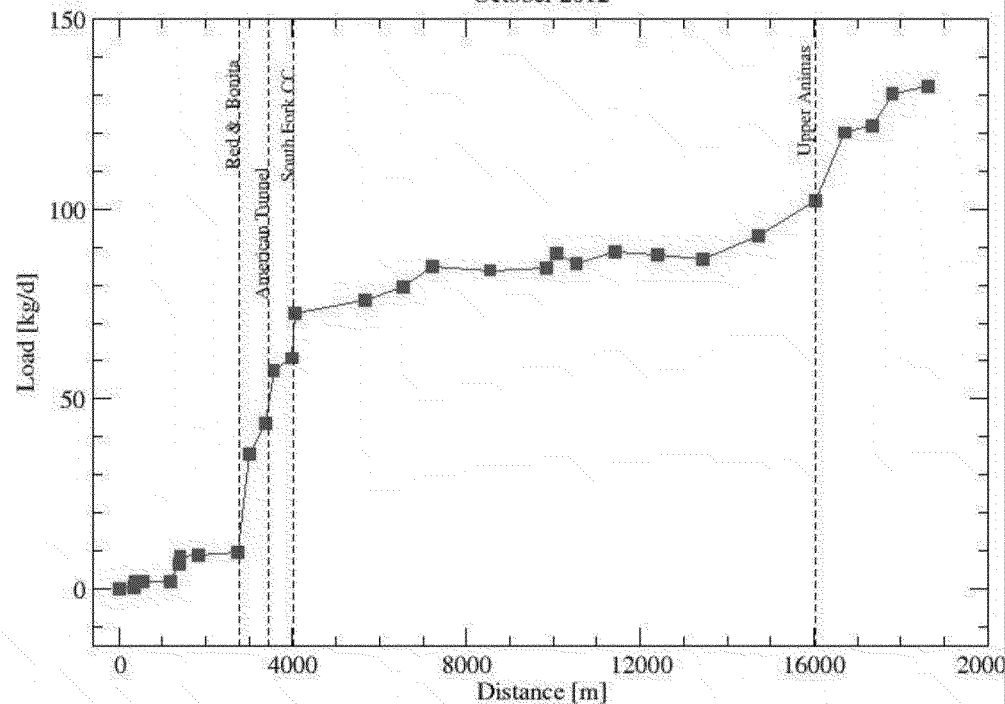
Dissolved Zinc

October 2012



Zn Load

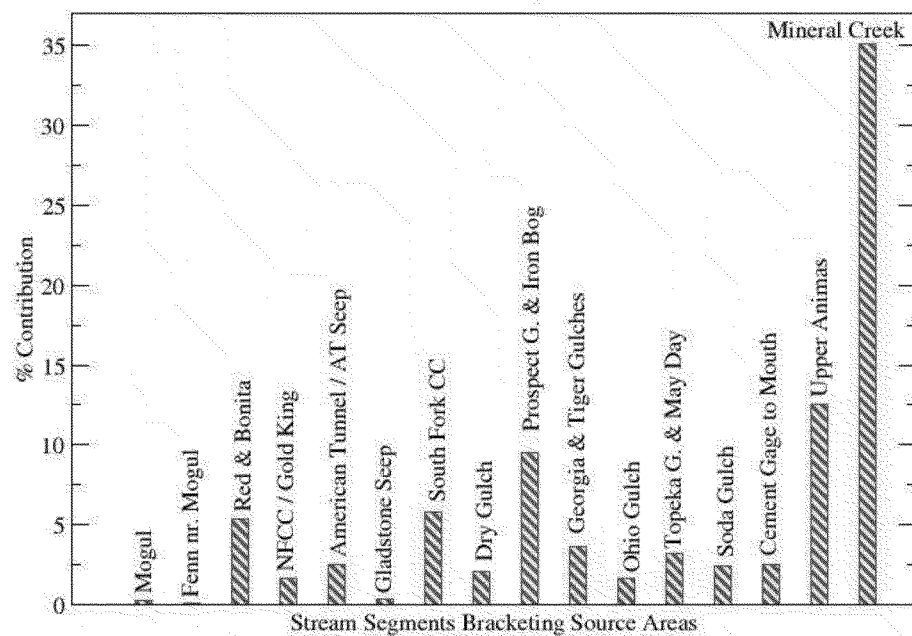
October 2012



# Part III: Results – Loads & Sources

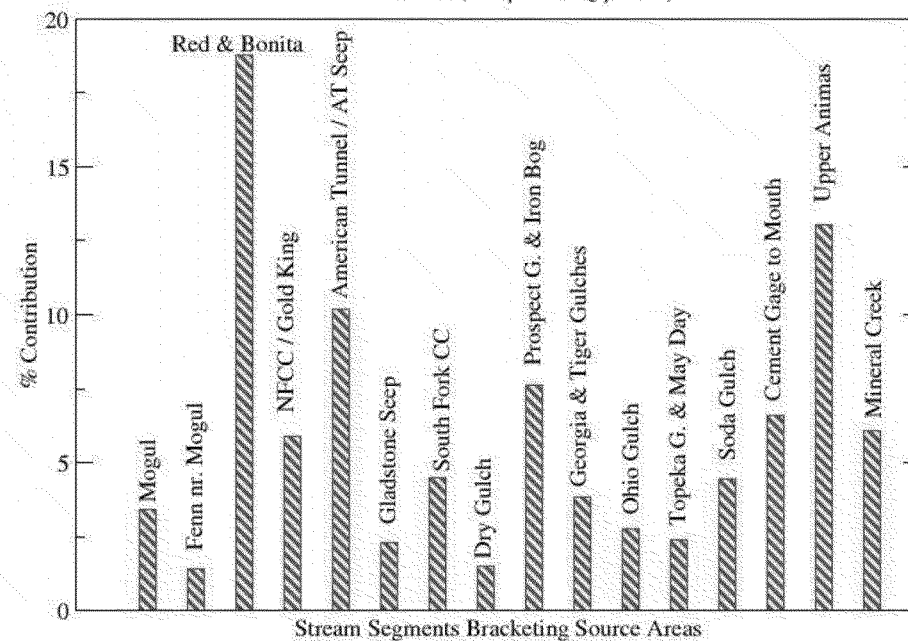
Percent Contribution to SO<sub>4</sub> load at A72

October 2013 (19 April 2013 Q)

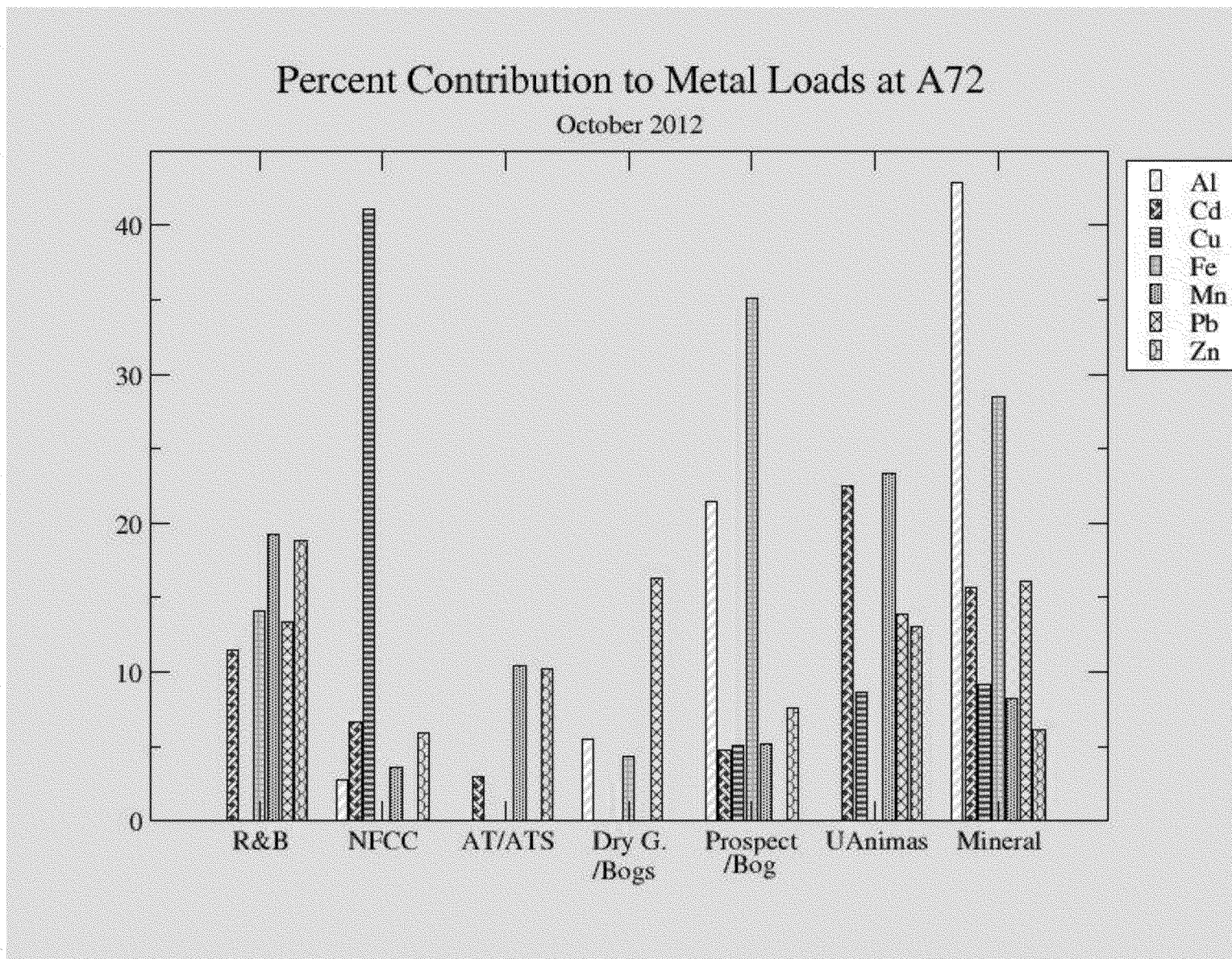


Percent Contribution to Zn load at A72

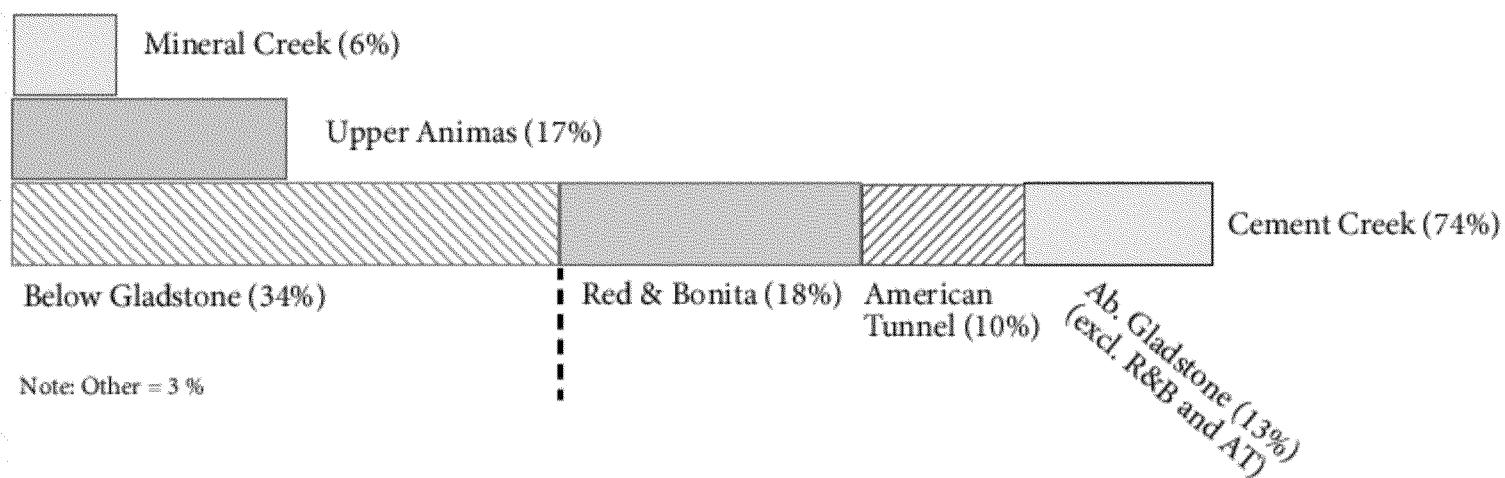
October 2012 (19Apr2013 Q profile)



# Part III: Results – Loads & Sources

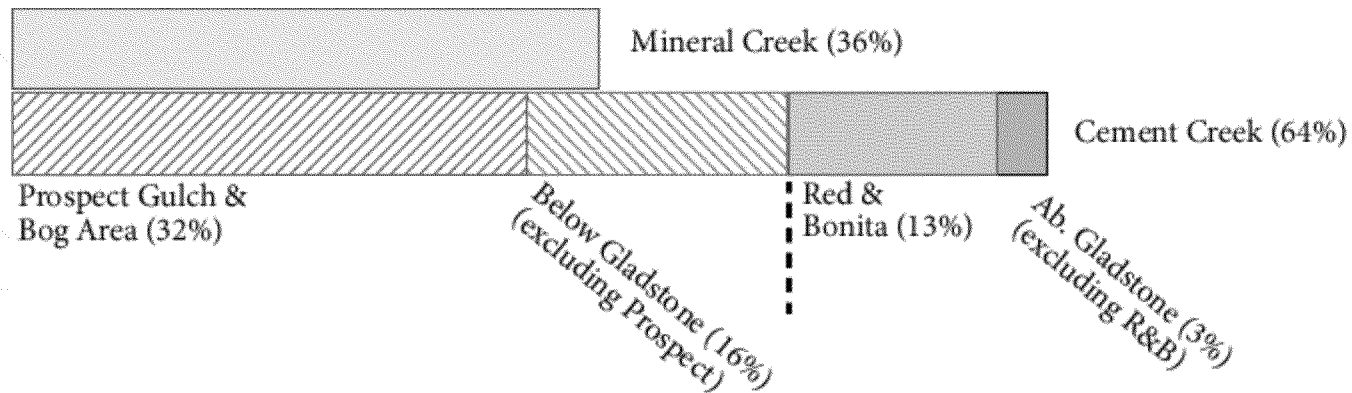


# Oct. 2012: Sources of Zinc



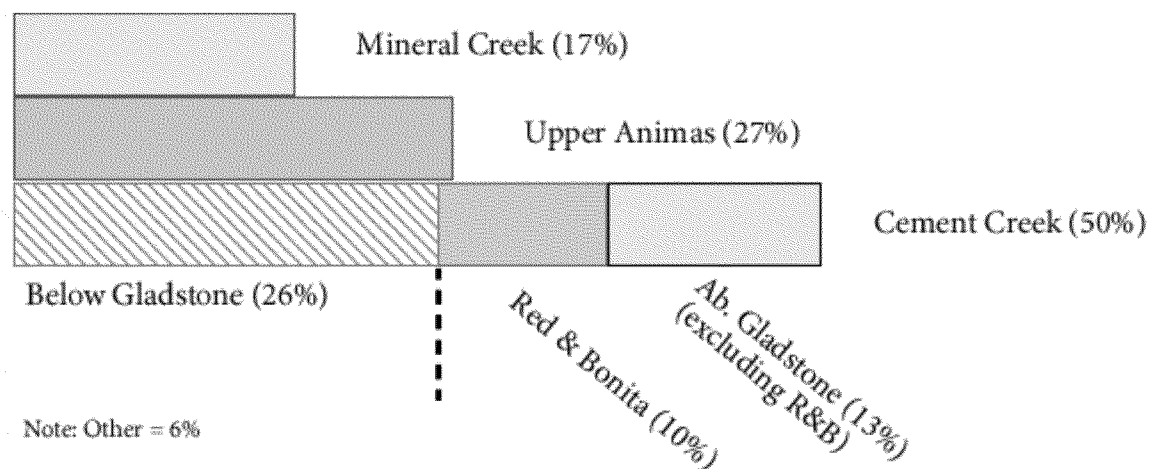
Focus Area: Upper Cement Creek

# Oct. 2012: Sources of Iron



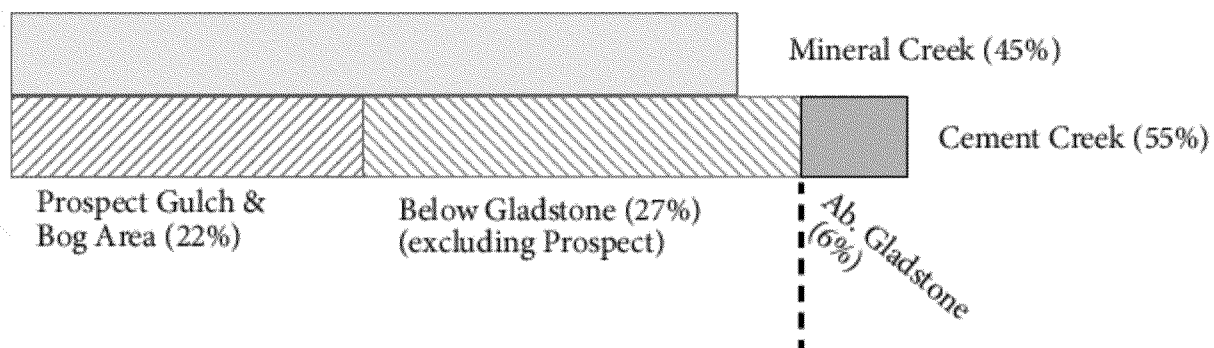
Focus Area: Lower Cement Creek

# Oct. 2012: Sources of Cadmium

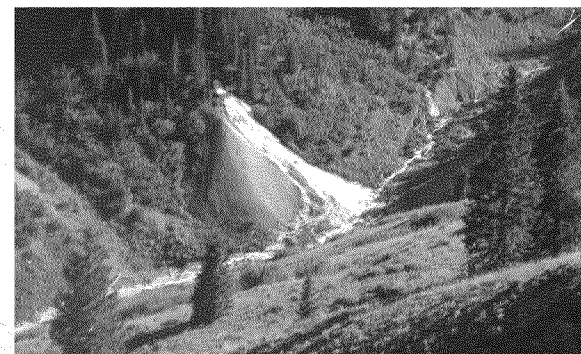


Focus Areas: Lower Cement Creek  
Upper Cement Creek  
Upper Animas

# Oct. 2012: Sources of Aluminum



Focus Areas: Lower Cement Creek  
Mineral Creek



# Part III Results:

## Reactive transport modeling

# Study Objective

- Main Objective:

Use a reactive transport model to evaluate remedial options for Cement Creek

- Data Requirements:

- Synoptic data set representing “steady-state” conditions
- Spatial profiles of streamflow and concentration

- Doing the 2-Step:

- Model Calibration: Reproduce existing conditions
- Prediction: Modify calibrated model to reflect remediation

# Model Calibration: Reproduce existing conditions

- **Components:**

- Al, As, Cd, Cu, Fe(II), Fe(III), H<sup>+</sup>, Ni, Pb, SO<sub>4</sub>, Zn, Ca, CO<sub>3</sub>

- **Reactions:**

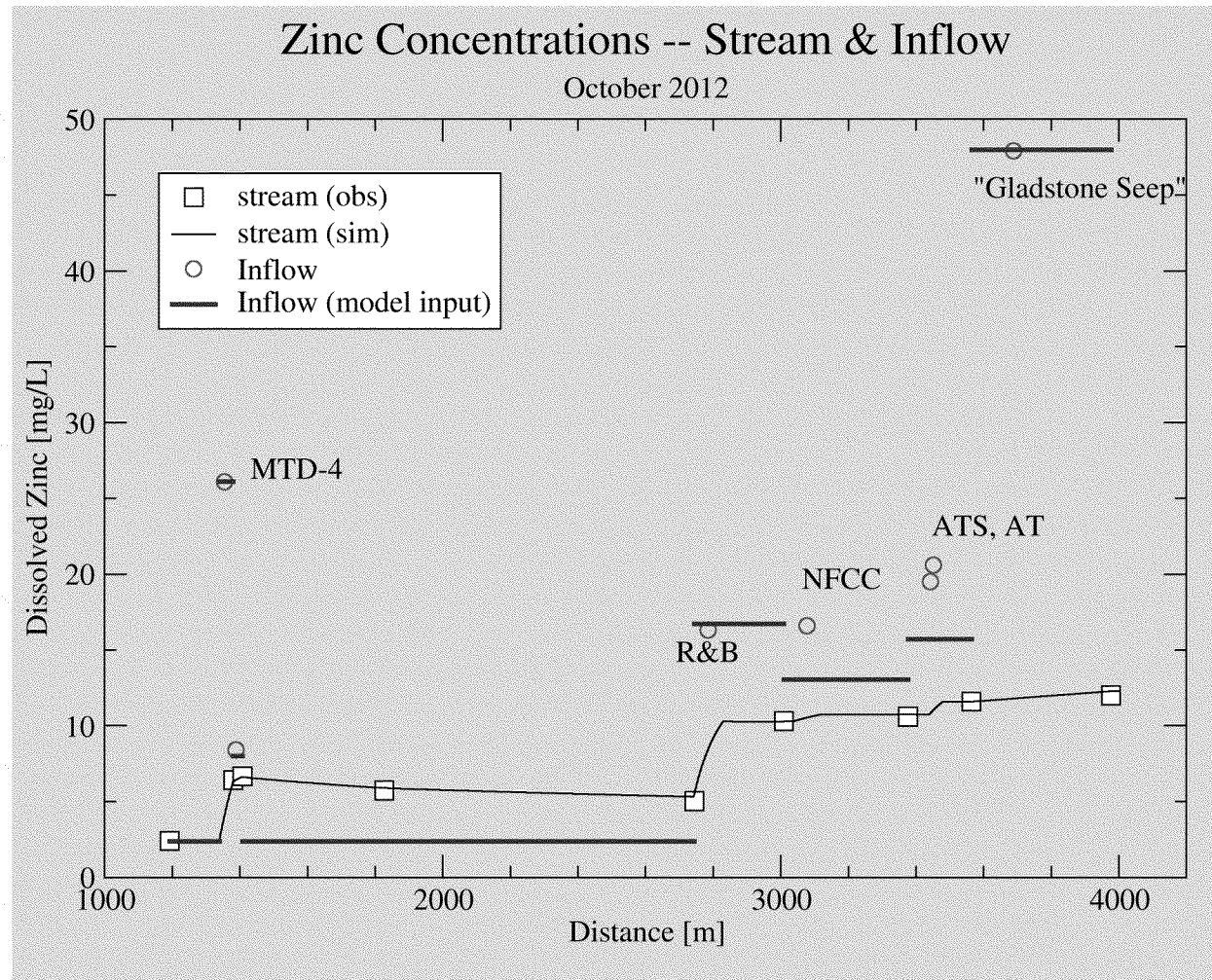
- precipitation: Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>
- sorption of As, Cd, Cu, Pb, and Zn onto HFO
- oxidation of Fe(II)
- degassing of CO<sub>2</sub>

- **Model Input:**

- spatial streamflow profile (1 flow / site based on QA)
- inflow chemistry (synoptic sampling)
- equilibrium constants (MINTEQ database)

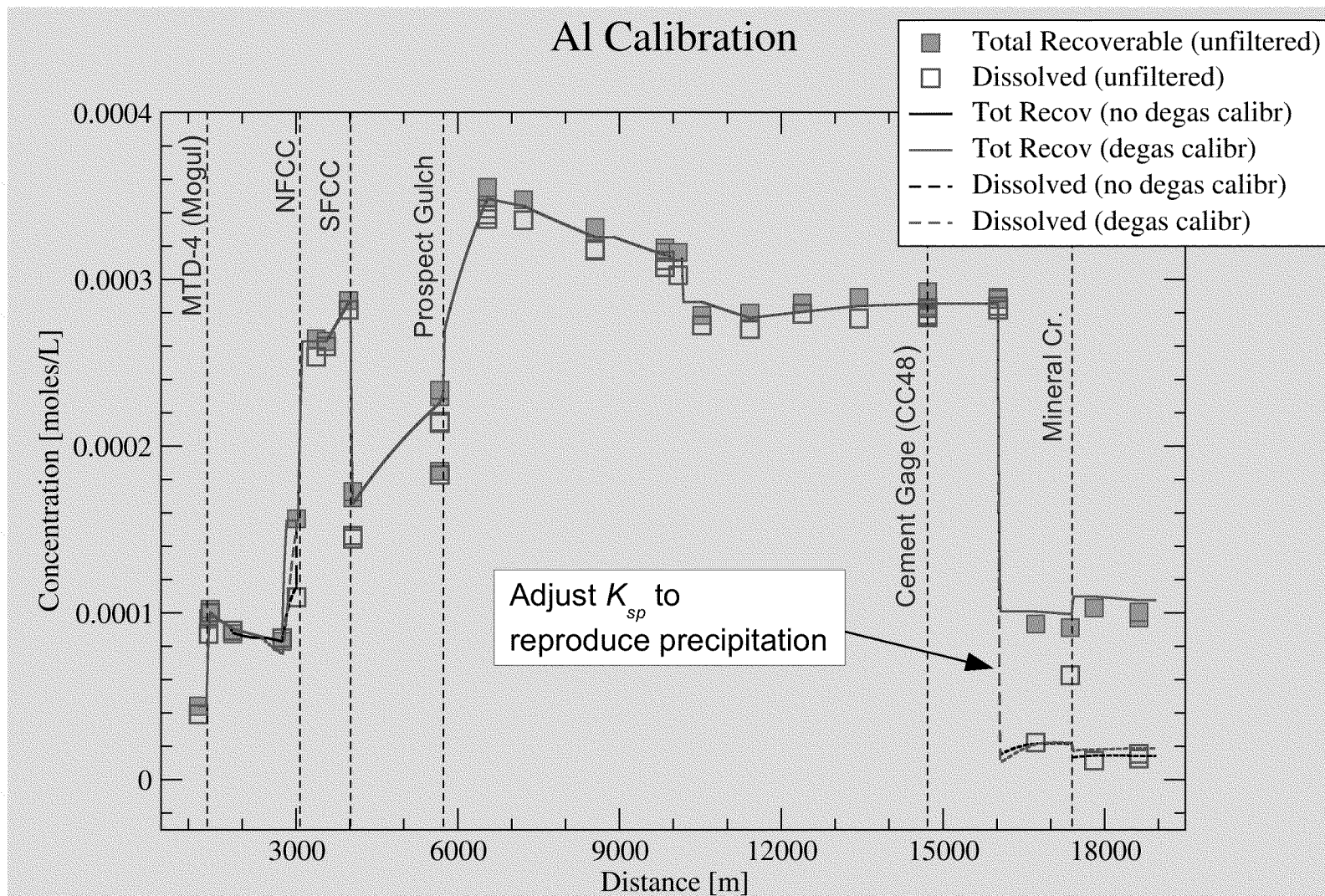
# Model Calibration: Inflow Chemistry ( $C_L$ )

Set  $C_L$  to reproduce stream data; Zinc input values realistic



# Model Calibration: Modify Reaction Constants

adjust  $\text{Al}(\text{OH})_3$   $K_{sp}$  to reproduce precipitation below Cement/Animas confluence



# Predicting Effects of Remediation

- Modify calibrated model to reflect proposed remedial action
- Remedial Scenarios:
  - Plug Red & Bonita Adit (100% reduction)
  - 1996 Treatment Plant Conditions

# Predicting Effects of Remediation

## ***Role of Uncertainty***

- Sources of Uncertainty:
  - Equilibrium “constants” describing precipitation and sorption vary over a wide range
  - degassing of CO<sub>2</sub> may or may not be an important process effecting pH
  - variation in low-flow water quality

# Role of Uncertainty

## Factor #1: Equilibrium Constants

- Solubility Products for Precipitation of Al & Fe
  - known to vary over a wide range
  - default values modified during calibration
- Surface complexation constants for sorption of As, Cd, Cu, Ni, Pb, Zn
  - defaults based on best estimates of Dzombak & Morel
  - default values modified during calibration
- Dealing w/ Uncertainty:
  - consider predictive simulations w/ both calibrated values and defaults

# Role of Uncertainty

## Factor #2: degassing effect on pH

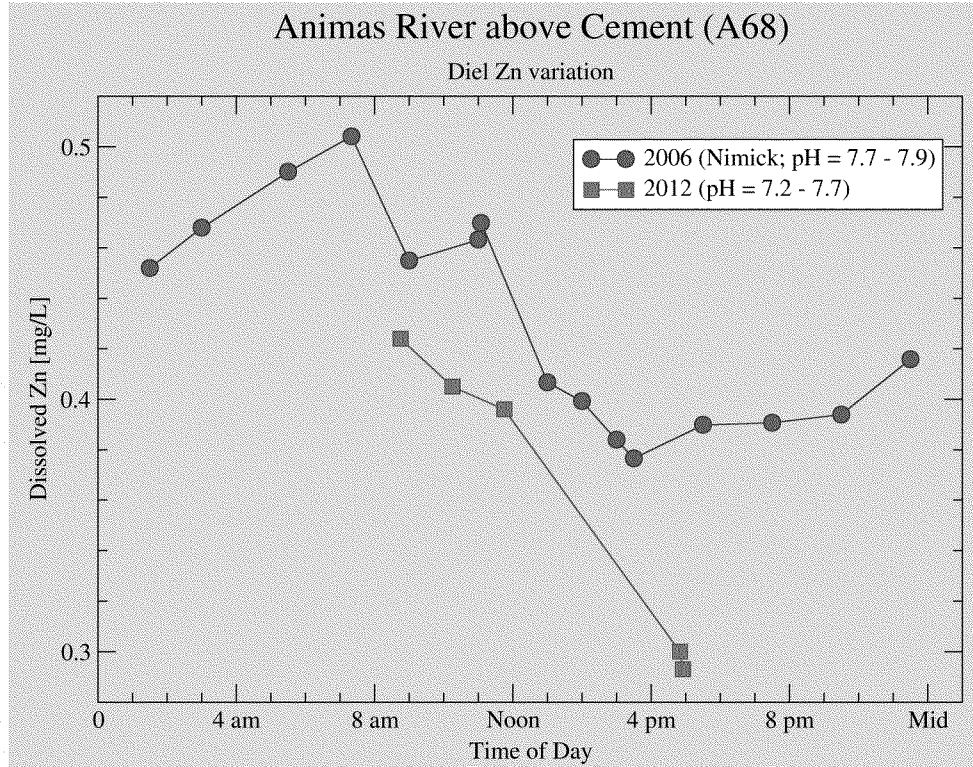
- pH can be difficult to measure; pH data are uncertain
- Calibrated models with and without degassing have been developed
- Dealing w/ Uncertainty:
  - consider predictive simulations w/ and w/o degassing

# Role of Uncertainty

## Factor #3: Variation in low-flow water quality

Inflow concentrations are set during calibration

Inflow concentrations are known to vary:



### Dealing w/ Uncertainty:

Conduct “worst case” simulations where Mineral Creek and Upper Animas inflow concentrations are set equal to the max concentrations (2006/2012)

# Dealing w/ Uncertainty

- Sensitivity Analysis
  - Equilibrium constants: calibrated vs. defaults
  - Degassing: with vs. without
  - Inflow concentrations: calibrated vs. worst case
- 8 simulations for each remedial scenario
  - provides range of possible outcomes
  - “best estimate” = calibrated degas model (B)
  - compare results based on median (M)

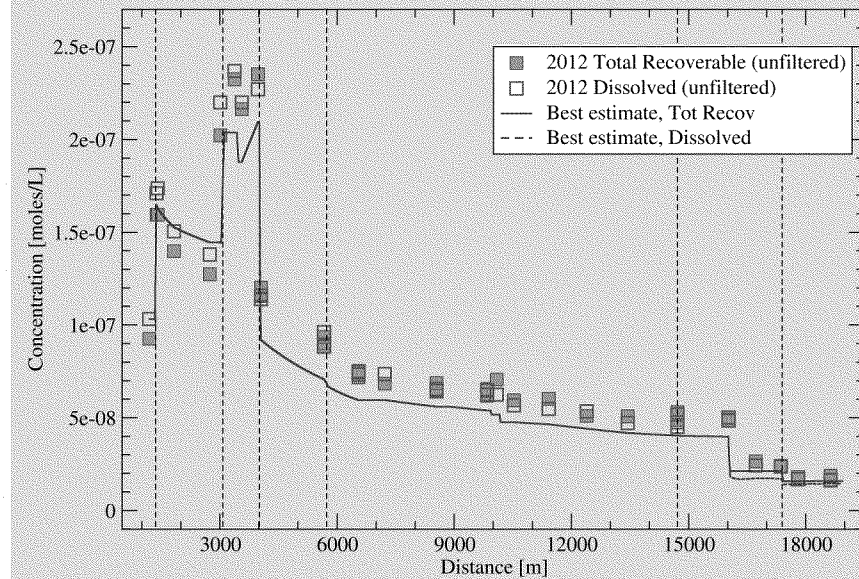
## Remedial Scenario #1: 100% removal of R&B load



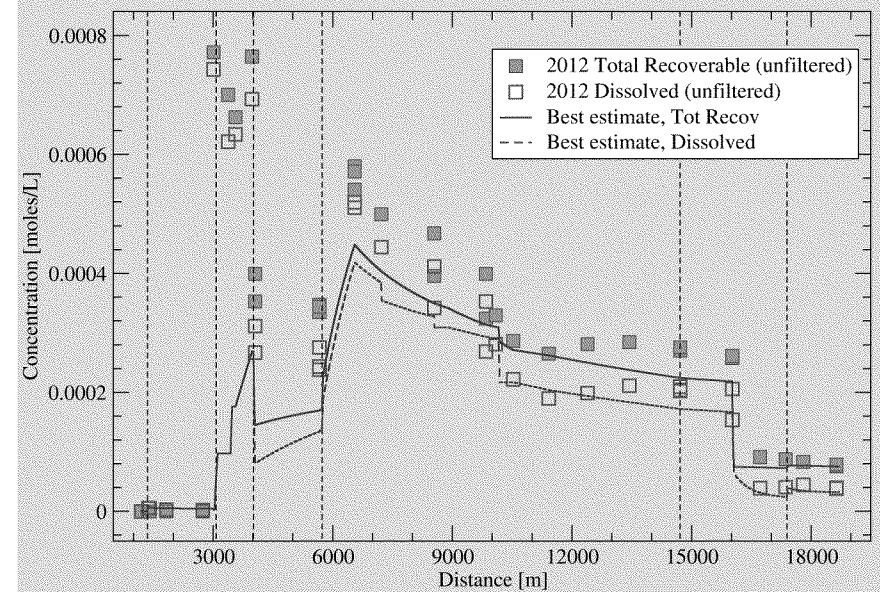
Modify the calibrated model such that no water enters between the two stream sites that bracket the Red & Bonita

# Results: 100% removal of Red & Bonita load

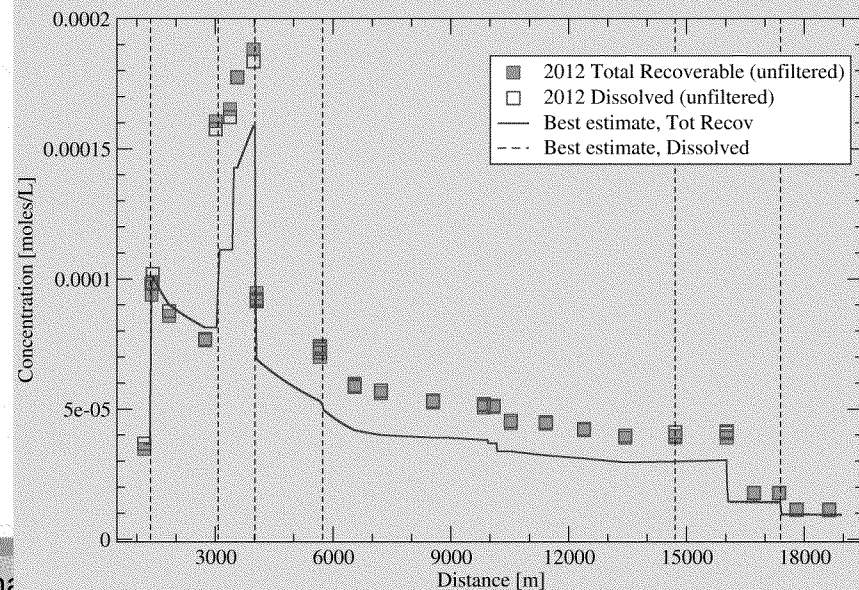
Cd, 100% Removal of Red & Bonita load



Fe, 100% Removal of Red & Bonita load

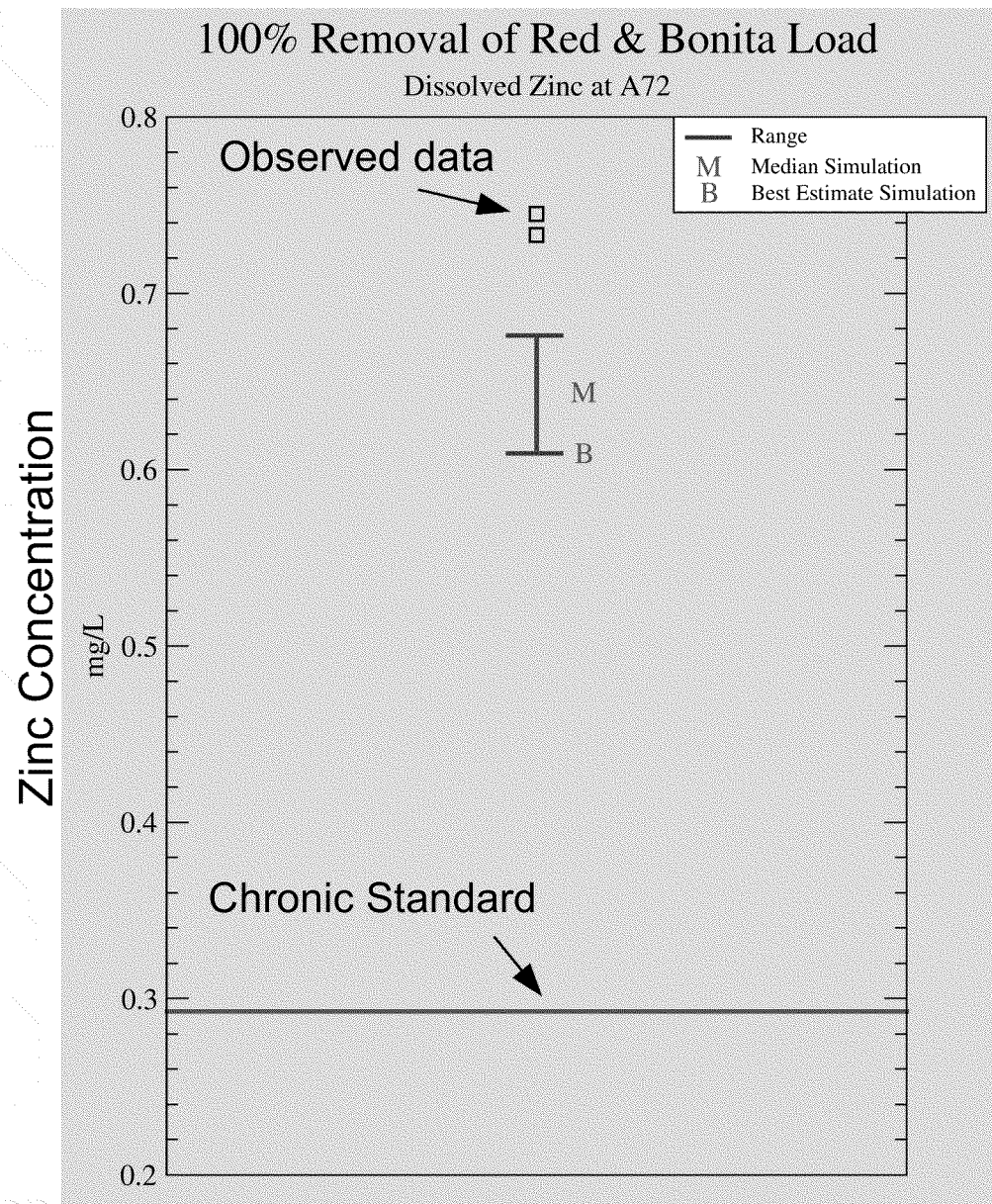


Zn, 100% Removal of Red & Bonita load



pH & Al – v. similar to existing conditions

# Results: 100% removal of Red & Bonita load



# Normalized Results

- Concentrations vary between constituents  
– normalize to allow for comparison

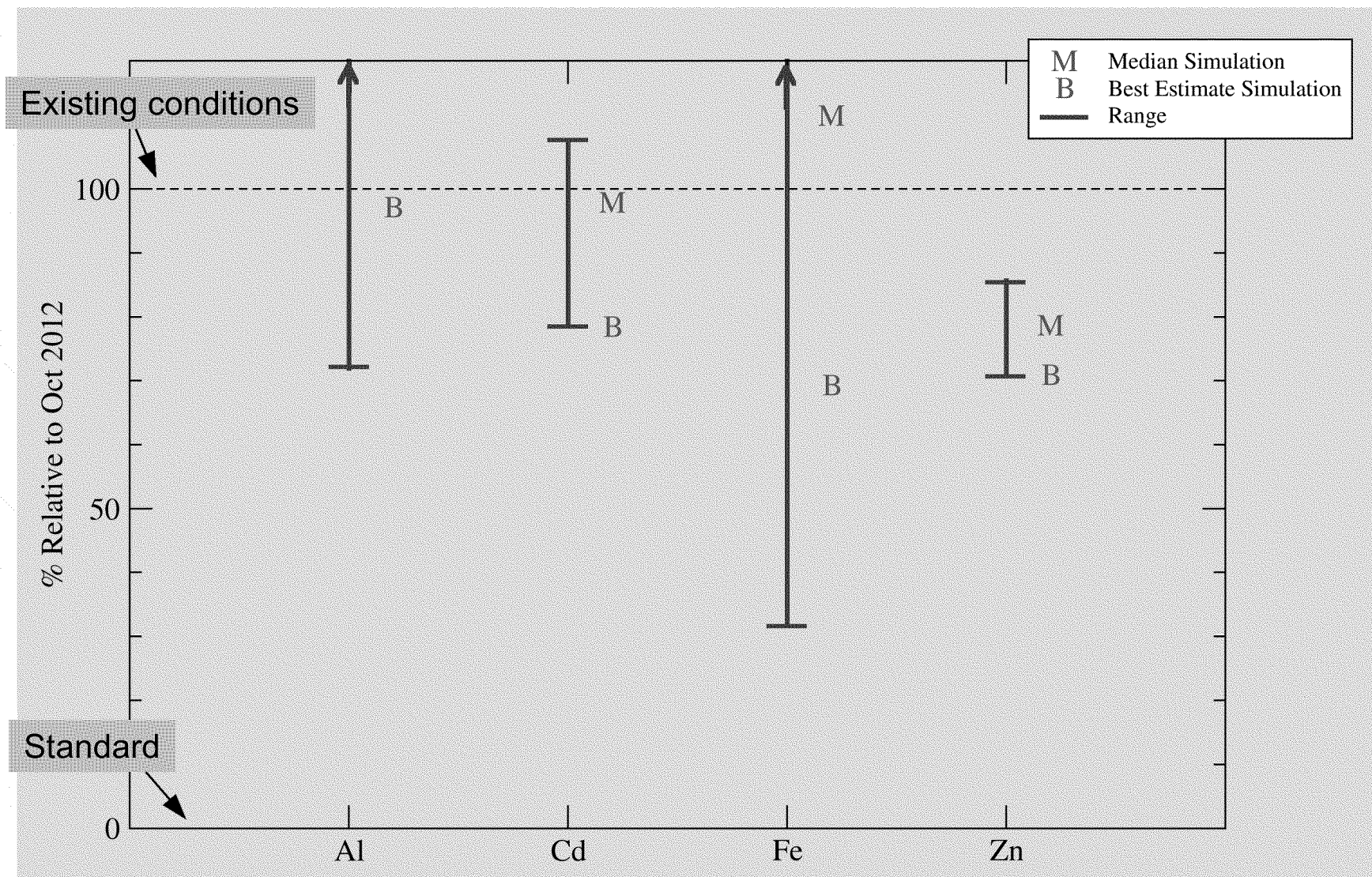
$$C_n = 100 * \frac{(\text{Prediction} - \text{Standard})}{(\text{Observed Data} - \text{Standard})}$$

If:

Prediction = Observed Data (2012)  $\rightarrow C_n = 100$

Prediction = Standard  $\rightarrow C_n = 0$

# Normalized Results: 100 % Removal of Red & Bonita load



Note: Al and Fe results assume all precipitated mass is removed (standards are in terms of totals; Cd is based on dissolved)

## Remedial Scenario #2: 1996 Treatment Conditions

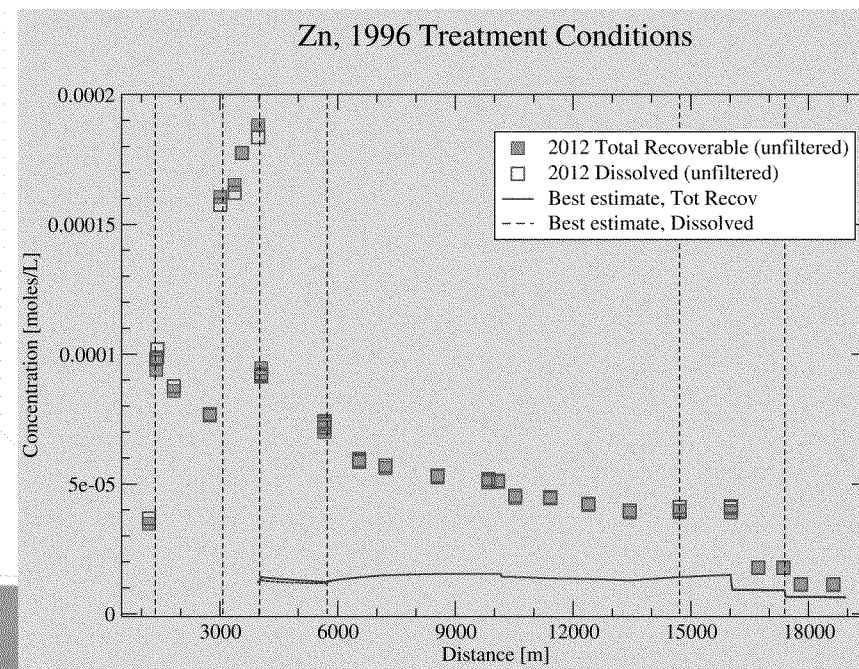
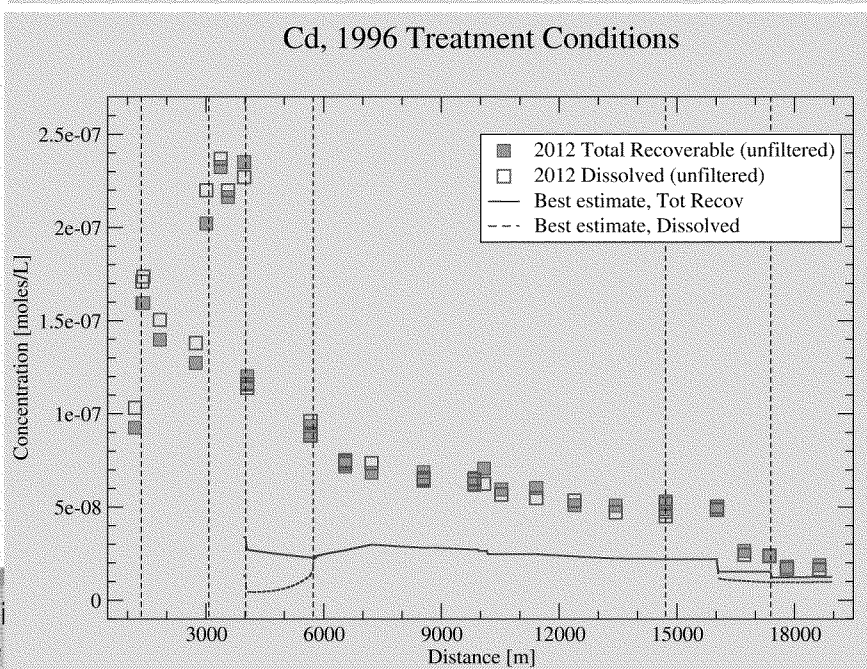
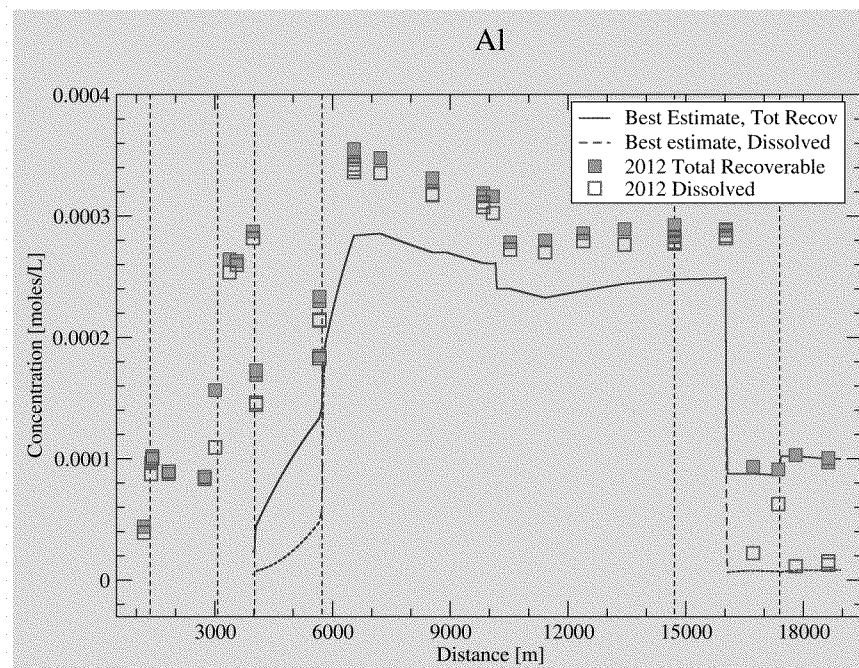
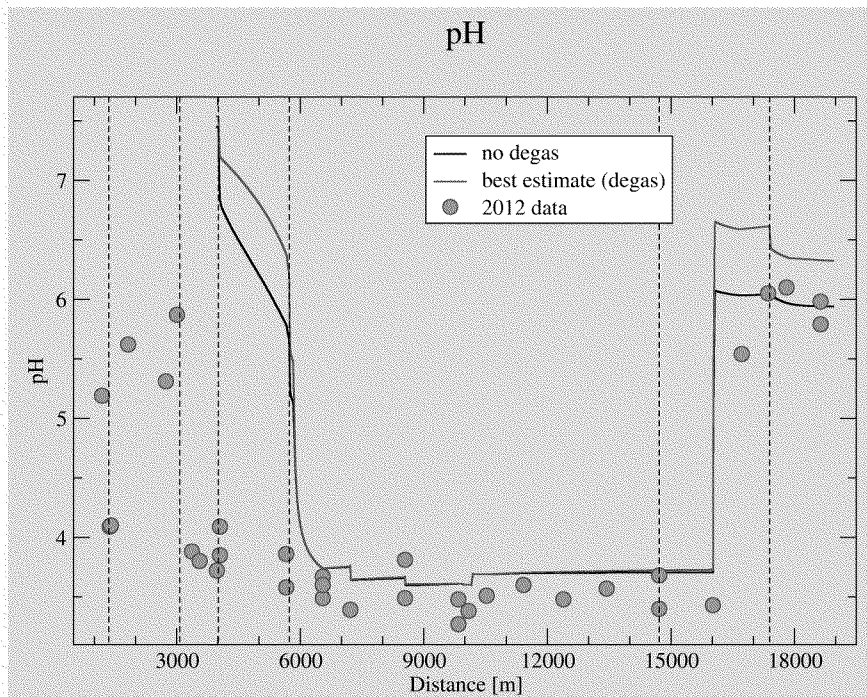


1996: Gladstone treatment system collected most of the water upstream of the South Fork

Move upstream boundary (above Mogul) to just above South Fork.

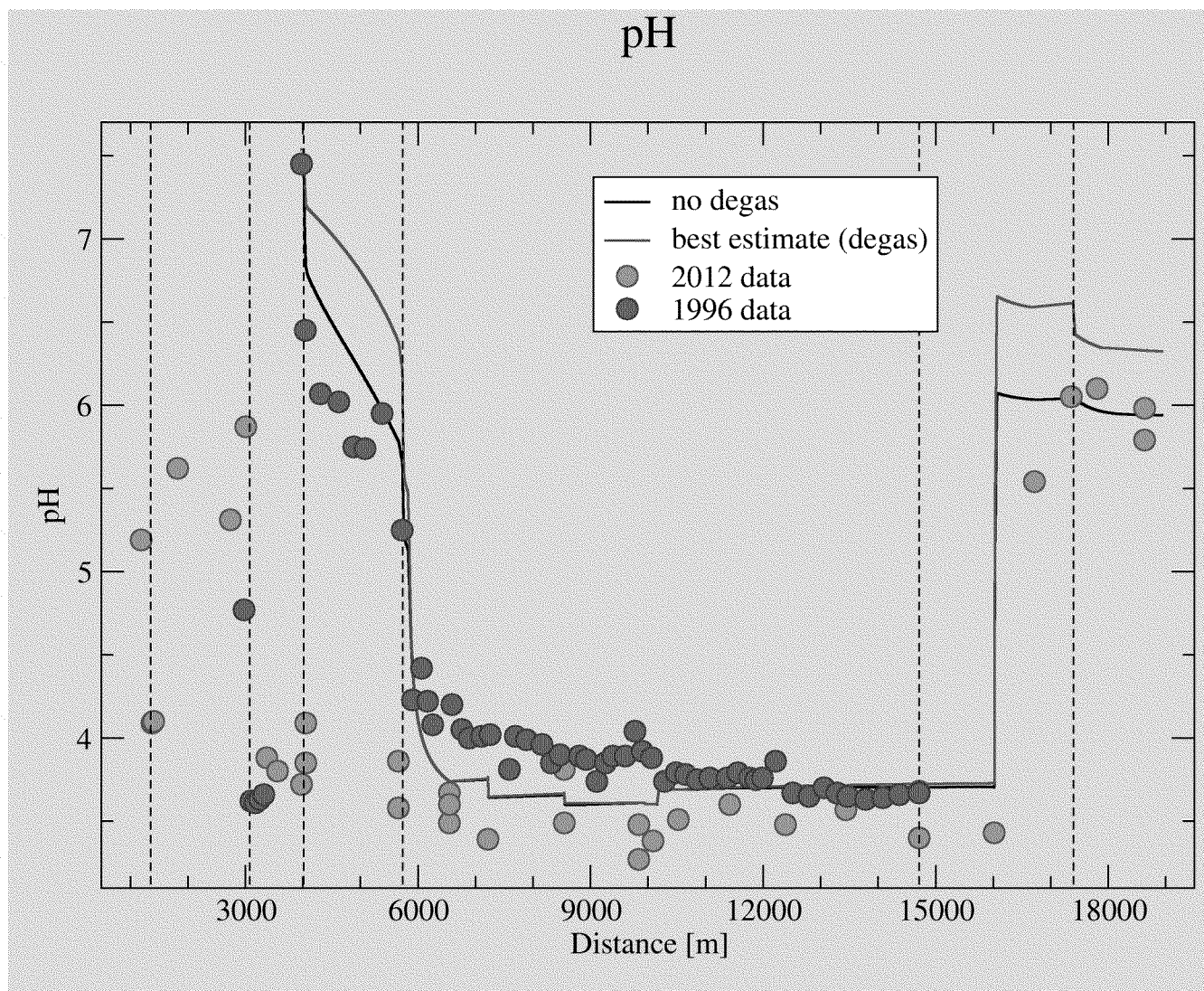
Specify upstream boundary chemistry based on 1996 data for Cement Creek, just downstream of the treatment system

# Results: 1996 Treatment Conditions

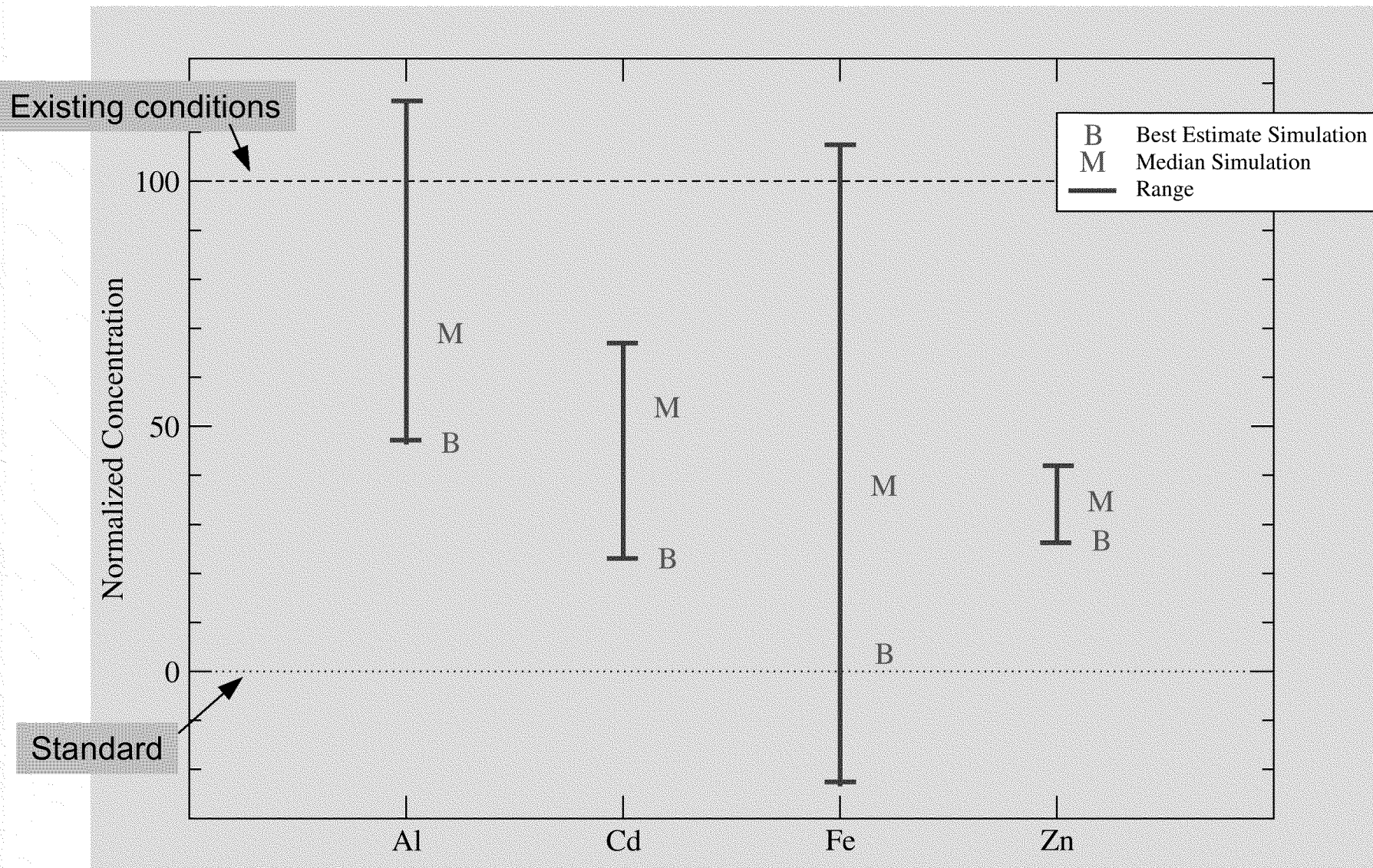


# Model “Validation”

## Comparison of Treatment Simulation w/1996 Data



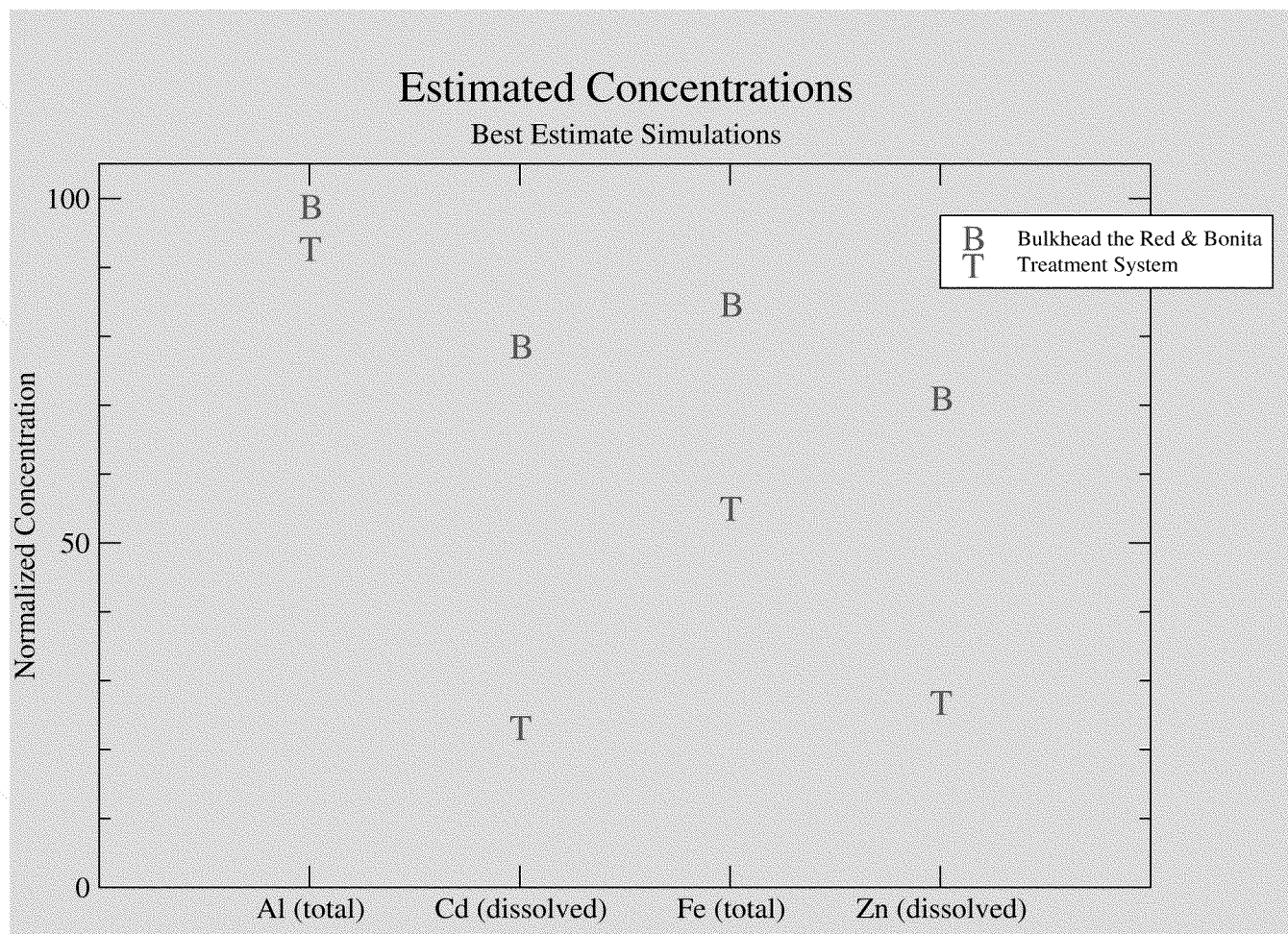
# Results: 1996 Treatment Conditions



Note: Al and Fe results assume all precipitated mass is removed (standards are in terms of totals; Cn is based on dissolved)

# Normalized Results, Revisited

## Best Estimate Simulations



# Summary

- Neither scenario results in the attainment of chronic water quality standards at A72
- Cement Creek is an appropriate focus for Fe & Zn
- Cd: need to consider Upper Animas
- Al: need to consider Mineral Creek